THE MANUFACTURE OF ACIDS AND ALKALIS
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Completely Revised and Rewritten under the Editorship of
ALEXANDER CHARLES CUMMING
O.B.E., D.Sc., F.I.C.

VOLUME V

The Manufacture of Hydrochloric Acid and Saltcake

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OF

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BY

ALEXANDER CHARLES CUMMING, O.B.E.

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EDITOR'S PREFACE

THE first English edition of Lunge's *Sulphuric Acid and Alkali* appeared in 1879. Since that date the book has been revised and extended in subsequent editions until, with the companion volumes on *Coal Tar and Ammonia*, it extended to nine volumes, covering most of the heavy chemical industries of Britain. A supplementary volume on Sulphuric and Nitric Acids by Dr Lunge in 1917 marked the end of his long labours in this field, and he informed the publishers that he could no longer undertake the preparation of new editions. The mere compilation of the volumes which he wrote would be in itself a wonderful achievement, but Dr Lunge's place in the history of chemical industry is due still more to the fact that he played a leading part in the discoveries and improvements which built up the industries of which he wrote.

By a curious coincidence, the end of Dr Lunge's long literary labours came just as the processes which he originally described died out. The Hargreaves process has gone, in this country at least; the Leblanc process is dying, if not actually dead already; even the chamber process for sulphuric acid has now a competitor that threatens to become a rival.

The volumes written by Dr Lunge have escaped a common criticism of factory managers that books give only an outline of a manufacturing process; indeed the only criticism has been that Dr Lunge's books gave almost too much detail. It may, however, be realised how important is a detail relating to a matter involving a possible saving of only one-tenth of one per cent., when it is pointed out that this small economy in the manufacture of sulphuric acid would mean a saving of thousands of pounds, since the value of the sulphuric acid manufactured annually in Great Britain alone amounts to several million pounds.

Each new edition of this series has been an expansion and extension of that which preceded it, fuller treatment being accorded to subsidiary manufactures as they increased in commercial importance, until the name *Sulphuric Acid and Alkali* became a cover for what was practically an encyclopedia of the heavy chemical industries.

The last arrangement into volumes and parts was largely fortuitous, having arisen from uneven growth of knowledge and commercial development in different branches, and as this appeared to be a favourable opportunity for instituting a new arrangement, it was decided to sub-divide the work into sections more in accord with modern developments. The last few years have brought with them so many changes in the chemical industries that the revision required in most of the volumes will involve such drastic recasting that the new edition will be more a new book than a revised edition.

It is doubtful if any one man could take up Dr Lunge's task of describing adequately all the industries now dealt with in these volumes, and it is certain that few would care to attempt it. Each volume will therefore be on a special subject and dealt with by a separate author who is responsible for that volume, and is given a wide discretion in his treatment of the subject.

The editor trusts that these united efforts will produce a new edition worthy of the great tradition which Dr Lunge has established.

The editor will be pleased to consider for publication in this series any manuscripts or original work on this or allied subjects.

A. C. C.

LIVERPOOL, *March* 1923.

AUTHOR'S PREFACE

SINCE the last edition of Dr Lunge's *Sulphuric Acid and Alkali* appeared, the industries connected with the manufacture of saltcake and hydrochloric acid have undergone such revolutionary changes that it has been a matter of great difficulty to decide what was a just balance between established but waning processes and those newer processes which are steadily supplanting them. The Hargreaves process is no longer in operation in this country, but its historical interest and its fascination for inventors justify a short chapter. The manufacture of saltcake by pan and furnace processes is still of sufficient importance to merit description, but these processes have been given in less detail than in former editions. As the old plant becomes worn out other methods of saltcake manufacture, having no connection with the Leblanc process, will probably be adopted, and fuller treatment has therefore been given to other methods and proposed methods.

An endeavour has been made to provide as full details as possible of the scientific data available regarding the properties of the chemical compounds used or prepared in these manufactures, as this information is of value whatever the method of manufacture may be.

The manufacture of hydrochloric acid is no longer necessarily connected with the manufacture of saltcake, and fuller treatment has therefore been given to its manufacture from chlorine and to other modern developments. The chapter on the theory of the absorption of hydrochloric acid has been completely ecast and rewritten, with elimination of much polemical natter of little modern interest.

The author desires to express his gratitude to the manu-acturers, works chemists, and friends who have kindly provided nformation, and also to Dr J. Knox for his assistance in the edious task of proof-reading.

A. C. C.

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THE MANUFACTURE
OF
SALTCAKE, GLAUBER'S SALT, AND HYDROCHLORIC ACID

INTRODUCTION

ONE of the outstanding features of the nineteenth century was the rise of several great chemical industries, and of these, one of the most important was the Leblanc soda industry. The fight for supremacy between it and its great rival, the Ammonia-soda industry, appeared likely to end with divided honours, but just as each appeared secure in its own field, the electrolytic process arrived and completed the downfall of the Leblanc process.

To the chemist there must be a natural regret that the day of the Leblanc process has passed. Originally a process for the manufacture of sodium carbonate and sodium hydroxide, it furnished so many intermediate and by-products that it gave directly or indirectly saltcake, hydrochloric acid, sodium carbonate, soda crystals, sodium hydroxide, Glauber's salt, the sulphide, sulphite, bisulphite, thiosulphate and hypochlorite of soda, chlorine and bleaching powder, Chance sulphur, and many other useful products. For many years before the war the Leblanc process held its own against the ammonia-soda process only on account of the value of these subsidiary products. With the extension of the electrolytic process for manufacturing caustic soda, and the manufacture of chlorine products from the electrolytic chlorine, the Leblanc process was steadily superseded.

The first stage of the Leblanc process was the manufacture of sodium sulphate (saltcake) and hydrochloric acid by the interaction of salt and sulphuric acid, or by the combined action of sulphur dioxide, oxygen, and water on salt. Although the Leblanc process as a method for the manufacture of alkali is almost, if not entirely extinct, the first stage is likely to retain an important position in chemical industry on account of the many uses of saltcake and hydrochloric acid.

It appears probable, however, that only so much hydrochloric acid will be made from salt and sulphuric acid as is produced in filling the demand for sodium sulphate, and that any additional hydrochloric acid required will be manufactured from electrolytic chlorine. The United States produced 168,000 short tons of hydrochloric acid in 1914, and Great Britain probably produced a little more, so that the manufacture of hydrochloric acid is in itself an important industry.

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CHAPTER I

PROPERTIES OF THE RAW MATERIALS AND PRODUCTS OF THE HYDROCHLORIC ACID AND SALTCAKE INDUSTRY

THIS chapter is devoted mainly to a description of the chemical and physical properties of sodium chloride, hydrochloric acid, and sodium sulphate, both as pure chemical substances and as more or less impure commercial products.

Hydrochloric acid, the only known compound of hydrogen and chlorine, has been known in the form of its solution ("spirits of salt") since the Middle Ages. The gas was first isolated by Priestley in 1772. Glauber in 1648 prepared hydrochloric acid by the action of sulphuric acid on common salt, and this is still the most important method of preparation. The other product of the reaction, "saltcake," was for long the only product of technical importance, and was manufactured on a very large scale even when hydrochloric acid was a useless and troublesome by-product. The chemical reaction involved in the manufacture is extremely simple:—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

We are concerned, therefore, mainly with the chemistry of these four substances. The chemistry of sulphuric acid is fully described in another volume. The chemical and physical properties of the other three compounds and of compounds closely related to them are described fully in the following chapter. Many details which may at present appear unimportant or irrelevant to the manufacturing process are included, because such information may at any time be found to have a direct bearing on technical problems connected with the manufacture.

RAW MATERIALS AND PRODUCTS

I. SODIUM CHLORIDE (*Common Salt*).

Formula: $NaCl$. It consists of 39·34 per cent. of sodium and 60·66 per cent. of chlorine.

Anhydrous sodium chloride crystallises in the regular system, nearly always in cubes. At temperatures above 0° it crystallises from solution in the anhydrous state; but the crystals, if rapidly formed, enclose a little mother-liquor, which causes decrepitation on heating.

For the absolute heat conductivity of rock-salt R. Weber[1] gives $K = 0{\cdot}0137$ at 0°.

Pure sodium chloride is practically non-hygroscopic, but crude salt is generally markedly hygroscopic on account of the presence of impurities such as magnesium chloride.

Pure sodium chloride does not absorb heat rays to any extent, 92 per cent. being transmitted and 8 per cent reflected.

Colloidal sodium chloride has been prepared by precipitation from organic solvents in absence of water.[2]

Density.—The density of pure sodium chloride is given by Clarke as 2·05-2·15; by Retger as 2·167 at 17°; by Krickmeyer as 2·174 at 20°. For rock-salt the values given vary between 2·14 and 2·24.

Refractive Index.—The average value given by a number of observers is 1·54432. Stefan (1871) gives 1·54412 at 18° for the D line.

Heat of Formation.—The heat of formation of anhydrous sodium chloride is given by Thomsen as 97,690 calories.

Double Chlorides.—According to O. Menge,[3] sodium chloride forms with magnesium chloride the compound $NaCl, MgCl_2$, and with calcium chloride the compound $CaCl_2, 4NaCl$.

Hardness of crystalline salt is stated to be 2·5.

Melting-point.—The melting-point of sodium chloride is given by Carnelley[4] as 772° C.; by Victor Meyer and Riddle[5] as 815·4°; by Lechatelier (1894) as 780°; by M'Crae (1895) as 811-814·5°; by Ramsay and Eumorfopulos (1896) as 792°; by Ruff and Plato (1903) as 820°; Huttner and Tamman (1905) as

---

[1] *Arch. sc. phys.*, 1895 (3), **33**, 590.

[2] Paal and Kuhn, *Ber.*, 1908, **41**, 51; P. von Weimarn, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 235.

[3] *Z. anorg. Chem.*, 1911, **72**, 162.

[4] *J. Chem. Soc.*, 1878, p. 280.

[5] *Ber.*, 1893, p. 2447.

810°; Arndt (1906) as 805°; U.S. Bureau of Standards (1919) as 810°. The solidifying-point according to Plato (1906) is 804·3°.

Boiling-point.—The boiling-point of sodium chloride is given by F. Emich[1] as 1750° and by L. H. Borgstrom[2] as 1490°. It volatilises noticeably far below the boiling-point, giving dense white fumes as the vapour condenses.

Density of Fused Salt.—The following figures are from determinations by Arndt and Gessler,[3] who give also the values for potassium chloride and various other chlorides:—

Temperature .	800°	850°	900°
Density . .	1·540	1·505	1·480

The densities of mixtures of fused sodium chloride with other chlorides agree with those calculated from the densities of the components.

Tin, zinc, lead, and copper oxides, and zinc, lead, and copper sulphides, are appreciably soluble in fused sodium chloride. Solution takes place very slowly, and even at 1200° the solubility does not reach 1 per cent.

Specific Heat.—For the specific heat between 13° and 46°, Kopp gives 0·213; between 15° and 98°, Regnault gives 0·2140°. For rock-salt at 0°, Weber gives 0·2146; between 13° and 45°, Kopp gives 0·219.

Solubility in Organic Solvents.—Turner and Bissett[4] give the following solubilities for sodium chloride in various alcohols, the figures representing grams of anhydrous salt dissolved by 100 g. of solvent at 25°:—

Solid Phase	Water	Methyl Alcohol	Ethyl Alcohol	Propyl Alcohol	Iso-amyl Alcohol
NaCl	36·05	1·31	0·065	0·012	0·002

The solubility increases rapidly if the alcohol is diluted with water. Other investigators, for example, found the solubility in 95·5 per cent. ethyl alcohol at 15° to be 0·172, and in 75 per cent. alcohol to be 0·7. It is appreciably soluble in glycerine.

Aqueous Solutions of Sodium Chloride.

Sodium chloride is readily soluble in water and the solubility curve is of rather an unusual type, the solubility varying very little with temperature. According to Bischof, the solubility does not vary with pressure up to 40 atmos. On dissolving 36 parts of salt in 100 parts of water at 12·6°, the temperature falls to 10·1°. The heat of solution of sodium chloride is given by Thomsen as −1180 cals. The heat of formation in solution is 81,510 cals. For its heat of formation by neutralisation, Thomsen gives—

---

[1] *Chem. Soc. Abstracts*, 1910, **98**, ii., 846.

[2] *Ibid.*, 1916, **110**, ii., 138.

[3] *Z. Elektrochem.*, 1908, **14**, 665.

[4] *Chem. Soc. Trans.*, 1913, **103**, 1904.

HCl, 200 mols. H_2O + $NaOH$, 200 mols. H_2O = $NaCl$, *Aq.* + 13,740 cals.

The solubility of sodium chloride in water has been determined with greater exactitude than that of most other salts. The following table gives a summary of the most reliable data:—

Temperature °C	Solid residue at the bottom	Parts by weight of NaCl to 100 H_2O	Observer
6·1	Ice	10·0	De Coppet.
6·6	"	11·0	Matignon.
9·25	"	15·0	"
12·7	"	20·0	"
16·66	"	25·0	"
21·2	Ice + $NaCl, 2H_2O$	28·9	Meyerhoffer and Saunders.
21·3	"	30·7	Matignon.
12·25	$NaCl, 2H_2O$	32·9	"
0·15	$NaCl, 2H_2O$	..	Meyerhoffer and Saunders.
0	$NaCl$	35·63	Andrea
10	"	35·69	"
20	"	35·82	"
30	"	36·03	"
40	"	36·32	"
50	"	36·67	"
60	"	37·06	"
70	"	37·51	"
80	"	38·0	"
90	"	38·52	Berkeley.
100	"	39·12	"
107·7	"	39·65	" B.-p. at 745 mm.
140		42·1	Tilden and Shenstone.
160	"	43·6	"
180	"	44·9	"

The most striking feature of the solubility curve for salt is the slight variation with temperature. The triple points are −0·15 and −21·3°. For freezing-point determinations, see F. E. E. Lamplough.[1]

The presence of other salts generally raises the solubility of sodium chloride, especially at a higher temperature. But his does not apply to other chlorides: thus NaCl is hardly oluble in a concentrated solution of magnesium chloride, and he chlorides of ammonium and potassium (also sodium nitrate) precipitate NaCl from its concentrated solutions. It is also ess soluble in hydrochloric acid than in water, and is almost completely precipitated from its aqueous solution by a current of HCl. Its solubility decreases with increasing concentration of HCl.[1] Sodium chloride, in general, shows no tendency to complex formation with other salts containing a common ion, and addition of a salt containing one of the ions of sodium chloride therefore causes a decrease in the solubility which is the more marked the greater the concentration of the salt added.

---

[1] *Proc. Camb. Phil. Soc.*, 1911. 16, 193.

The *freezing-points* of solutions of sodium chloride, according to Karsten, are:—

NaCl per cent	Freezing-point	NaCl per cent	Freezing-point
	Degrees		Degrees.
1	0·76	14	10·29
2	1·52	15	19·99
3	2·28	16	− 11·69
4	3·03	17	12·39
5	3·78	18	13·07
6	4·52	19	13·76
7	5·26	20	14·44
8	5·99	21	15·11
9	6·72	22	15·78
10	7·44	23	16·43
11	8·16	24	17·1[illegible]
12	8·88	25	17·77
13	−9·59	26	− 18·42

From Bischof's observations Karsten calculates the following figures for the *evaporation of solutions of sodium chloride* in comparison with pure water at temperatures from 7·5° to 90°. If from pure water in a certain time there is an evaporation of *one* volume of water, the evaporation from brine, under exactly similar conditions, is as follows:—

From 5 per cent. NaCl solution 0·8768 vols.
" 10 " " 0·7780 "
" 15 " " 0·7044 "
" 20 " " 0·6583 "
" 25 " " 0·6429 "

---

[1] Ditte, *Comptes rend.*, 1881, p. 156.

In other words, the quantity of heat which will evaporate one volume of water from pure water will only evaporate the amounts shown in the table from salt solutions.

Boiling-points of solutions of sodium chloride at a pressure of 760 mm. (Karsten):—

NaCl per cent.	Boiling-point.	NaCl per cent.	Boiling-point.	NaCl per cent.	Boiling-point.
	Degrees.		Degrees.		Degrees.
1	100·21	11	102·66	21	105·81
2	100·42	12	102·94	22	106·16
3	100·64	13	103·23	23	106·52
4	100·87	14	103·53	24	106·89
5	101·10	15	103·83	25	107·27
6	101·34	16	104·14	26	107·65
7	101·59	17	104·46	27	108·04
8	101·85	18	104·79	28	108·43
9	102·11	19	105·12	29	108·83
10	102·38	20	105·46	29·4	108·99

The last figure of the table refers to a saturated solution which boils at 108·99° under ordinary atmospheric pressure and contains 29·4 per cent. of salt.

Specific Gravities of Solutions of Sodium Chloride.

Per cent. NaCl.	Spec grav at $\frac{15^\circ}{15^\circ}$ (Gerlach)	Spec grav at 20 (Schiff)	Per cent NaCl	Spec grav at $\frac{15^\circ}{15^\circ}$ (Gerlach).	Spec grav at 20° (Schiff).
1	1·00725	1·0066	15	1·11146	1·1090
2	1·01450	1·0133	16	1·11938	1·1168
3	1·02174	1·0201	17	1·12730	1·1247
4	1·02899	1·0270	18	1·13523	1·1327
5	1·03624	1·0340	19	1·14315	1·1408
6	1·04366	1·0411	20	1·15107	1·1490
7	1·05108	1·0483	21	1·15931	1·1572
8	1·05851	1.0556	22	1·16755	1·1655
9	1·06593	1·0630	23	1·17580	1·1738
10	1·07335	1·0705	24	1·18404	1·1822
11	1·08097	1·0781	25	1·19228	1·1906
12	1·08859	1·0857	26	1·20098	1·1900
13	1·09622	1·0934	26·4	1·20433	...
14	1·10384	1·1012	27	...	1·2075

Heat-capacity and heat-conductivity of salt solutions according o Karsten (approximate values):—

NaCl per cent.	Heat-capacity.	Heat-conductivity.
0	1·0200	1·0000
5	0·9707	1·0302
10	0·9408	1·0629
15	0·9102	1·0987
20	0·8784	1·1384
25	0·8453	1·1830

Contraction in Volume on Solution.—There is a noticeable contraction in volume when salt dissolves in water. For data, see Hallwachs,[1] Wade,[2] and Happart.[3]

The *heat of formation* of a gram mol. (58·5 g.) NaCl from Na and Cl is in the solid state +97,690 cals. The heat of neutralisation of 40 g. NaOH with 36·5 g. HCl in the presence of 400 mols. of water is +13,740 cals. The heat of solution of 1 mol. NaCl in 200 mols. H_2O is −1180 cals.

Chemical Reactions of Sodium Chloride.

Sodium chloride shows little tendency to decompose or dissociate even on the strongest heating. It is decomposed by steam to an extremely small amount, the hydrolysis taking place only to a small extent when steam is blown through molten salt at a temperature approaching its boiling-point. In spite of this many patents utilise the supposed reaction.

When heated in presence of air or oxygen to a very high temperature, sodium chloride evolves some chlorine.[4] It cannot be reduced by heating in hydrogen.

Molten anhydrous sodium chloride is readily decomposed by electrolysis, and sodium is prepared on a large scale in this way. Aqueous solutions of salt are also decomposed on electrolysis, yielding sodium hydroxide and chlorine. This method for preparing caustic soda is already of great importance and it may yet replace all other methods.

When repeatedly evaporated with nitric, oxalic, and many other acids, sodium chloride is completely converted into a salt of the acid with evolution of hydrochloric acid.

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[1] *Wied. Ann.*, 1894, **58**, 1.

[2] *Trans. Chem. Soc.*, 1899, **75**, 254.

[3] *Bull. Inst. Liège*, 1903.

[4] de Sanderval, *Comptes rend.*, 1893, **116**, 641.

Sodium chloride absorbs a considerable amount of sulphur trioxide,[1] and only on heating is there evolution of gas. The reaction which occurs is represented by the equation:—

$$NaCl + 2SO_3 = NaOS_2O_5Cl.$$

When sodium chloride is warmed with sulphur trioxide, the following reaction takes place:—

$$2NaCl + 4SO_3 = Na_2S_2O_7 + S_2O_5Cl_2.$$

When sulphur trioxide vapour is led over red-hot sodium chloride, sulphate is formed:—

$$2NaCl + 2SO_3 = Na_2SO_4 + SO_2 + Cl_2.$$

If a solution of sodium chloride is saturated with hydrogen sulphide, sodium sulphide up to 15 per cent. is formed, and by passing steam and hydrogen sulphide over salt the decomposition can be carried even further.

When lead oxide is added to fused salt, caustic soda and lead chloride are formed. When fused salt is strongly heated with lead, metallic sodium and lead chloride are said to be produced.

Occurrence of Sodium Chloride in Nature.[2]

Sodium chloride is found in nature more widely distributed and in larger quantity than any other soluble salt of the alkali metals. It is the chief solid constituent present in sea-water, in the water of salt lakes, natural brine, and in rock-salt. It occurs also as a deposit on salt deserts and in salt clay. The detailed description of the manufacture of salt from these sources is outside the scope of this volume, but a few notes may be of use. Analyses are also given in order to show the nature of crude salt which may be met with in practice.

In *sea-water* sodium chloride forms about four-fifths of the solid constituents. Its absolute quantity in the open ocean varies between 28 and 36 g. per litre, usually 33 g.; in the Baltic we find only 4·8, in the Black Sea 15·9 g. In many places in warm climates salt is recovered from sea-water by spontaneous evaporation in the air, especially in France, Italy, Spain, Austria (in the Adriatic), South Russia (Crimea), and other localities.

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[1] W. Traube, *Ber.*, 1913, 46, 2513.

[2] A very detailed description of the occurrence and manufacture of technical sodium chloride, from the pen of Ochsenius and Furer, is found in the fourth German edition of Muspratt's *Chemistry*, by Prof. Bunte, vol. vi., pp. 431-840 (of 1898). This is referred to in the text as "Muspratt-Bunte."

The manufacture of salt from sea-water is, in theory, a very simple affair, but it is made difficult by the very large quantities of water that have to be treated, the enormous area necessary for such large scale solar evaporations, and the difficulty of keeping the crystallised salt free from the mother-liquor salts. In exceptional cases these are also taken into the cycle of operations, and magnesium sulphate, Glauber's salt, potassium chloride, magnesium chloride, etc., are made from them. The industry of making salt from sea-water is minutely described in the French edition of this book[1] and in Lunge's paper on the saltworks at Giraud-en-Camargue[2]; also in Muspratt-Bunte, vi., pp. 594 *et seq.* The following are analyses of a number of samples of sea-salt :—

Analyses of Sea-salt (from Muspratt-Bunte, vi., p. 605).

No	NaCl	$MgSO_4$	$MgCl_2$	$CaSO_4$.	$NaSO_4$	Insoluble.	H_2O.
1	95·91	...	0·46	0·49	0·40	0·16	2·58
2	96·35	...	0·50	0·45	0·51	0·07	2·12
3	95·19	1·69	...	0·56	..	...	2·45
4	89·19	6·20	...	0·81	. .	0·20	[illegible]
5	80·09	7·27	...	3·57	..	0·20	8·36
6	91·14	3·54	0·70	0·33		...	4·20
7	93·17	3·50	1·10	1·50	..	0·20	...
8	98·80	0·50	0·50	0·10	.	0·10	...
9	93·65	1·75	2·80	1·50	...	0·40	...
10	96·50	0·25	0·32	0·88		0·10	1·95
11	95·86	0·35	[illegible]	1·30	...	0·15	2·10
12	92·46	0·66	0·55	2·28	.	[illegible]	3·10
13	96·42	0·42	0·20	1·95	...	1·00	...
14	97·20	0·50	0·40	1·20	. .	[illegible]	...
15	95·11	1·30	0·23	0·90	.	0·10	2·35
16	87·97	0·50	1·58	1·65	...	0·80	7·50

1, Salt from S. Felice, near Venice (Schrötter & Pohl); 2, from Trapani, Sicily (the same); 3, from St Ubes, Portugal, I*a* quality (Berthier); 4, ditto, II*a* quality; 5, ditto, III*a* quality; 6, from Figueras, Portugal (Berthier); 7, from Lymington (Henry); 8, ditto, "cat-salt"; 9, Scotch sea-salt (Henry); 10 to 12, from St Ubes (Karsten); 13 and 14, from Oléron and Marennes, Charente-Inférieure; 15, ordinary salt from Languedoc and Bretagne; 16, grey salt from Bretagne.

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[1] Lunge et Naville, *Traité de la fabrication de la Soude*, vol. ii., pp. 27-46.

[2] *Chem. Ind.*, 1883, p. 225.

The following analyses were made by Naville of the average products obtained in actual work at the Salins du Midi, from the Étang de Berre:[1]—

	First quality. (Kitchen salt.)	Second quality. (Manufacturing salt.)	Third quality. (For curing fish.)
$CaSO_4$	1·115	0·621	0·440
$MgSO_4$	0·221	0·506	0·612
KCl	...	traces	0·122
$MgCl_2$	0·100	0·377	1·300
Insoluble	0·050	0·030	0·050
Water	1·400	4·201	5·758
NaCl	97·100	94·212	91·217
	99·986	99·947	99·499

Rock-salt occurs in all geological formations, most abundantly in the Permian, Trias, Jura, and Chalk. The best-known occurrences are:—in the Permian, the great Stassfurt bed; in the Upper New Red Sandstone, many German and most English brine-springs; in the Muschelkalk, most of the South German and Austrian beds (Friedrichshall, Schwäbischhall, Salzkammergut, Berchtesgaden, Reichenhall); in the Keuper, the Lorraine beds (Dieuze, Vic, Nancy); in the Nummulite Limestone, the salt mountain at Cardona, in Spain, 300 feet high, and the Asia Minor beds; the Tertiary formation yields the large beds in the Carpathians (Wieliczka), in Hungary (Marmaros), and in the Russian plain. An enormous salt bed was discovered in Utah in 1907.

The table on p. 13, from Muspratt-Bunte, vi., p. 437, gives the composition of samples of rock-salt from various localities. The tables on p. 14 contain some further analyses.

Steppe-salt, as efflorescences on the ground of steppes and deserts, is found in the Soudan, in Central Asia (Thibet), near the Caspian Sea, the deposits being merely of local importance.

Salt lakes exist in rather large numbers; their water, apart from sodium chloride, always contains many other salts, especially calcium and magnesium chlorides, sulphates, etc. Among the best known are the Great Salt Lake in Utah (with 9·74 per cent. NaCl), the Titicaca Lake, 18,800 feet above the sea-level,

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[1] Lunge et Naville, Vol. ii., p. 46.

No.	NaCl.	MgCl$_2$.	CaCl$_2$.	Na$_2$SO$_4$	CaSO$_4$.	Fe$_2$O$_3$.	Bitumen and clay	Insoluble	CaCO$_3$.	MgCO$_3$.	MgSO$_4$.	KCl.
1	97·8	..	...	...	0·3		1·9	...	...	...	...	...
2	98·32	0·18	0·21	..	0·62		..	0·31	...	...	...	...
3	98·3	0·05	...	..	0·65		.	1·08	...	...	...	...
4	98·04	0·06	0·41	.	1·49			..	..	...	...	...
5	98·55	0·01	0·99	.	0·44	..	.	...	.	...	...	...
6	99·03	..	..	.	..		.	0·97	..	...	...	...
7	99·97	...	...		0·02		0·01	...	...	...	...	...
8	98·36	...	...	0·03	0·55		0·58		0·52	0·13	...	..
9	98·81	..	0·02		0·11		0·80		0·16	0·15	...	...
10	90·98	...	..	.	...	.		..	.	...	9·02	...
11	100·00	trace	.	.	...		.		...	..	...	...
12	99·85	0·15	trace		.	..		.	...	...	...	...
13	99·92	0·07	..	..		..	...	...	..	..	...	...
14	99·43	0·12	0·25	..	0·20		..	.	..	...	.	...
15	98·14	...	..	..	1·86	.		...	..	...	...	..
16	99·63	...	0·28	.	...	..		..	...	...	...	0·09
17	25·09 to 94·07	0 to 5·02	...	0 to 1·57	0·89 to 7·04	0 to 1·2		0 to 2·23	...	...	0 to 42·07	...
18	98·3	0·2	0·2	..	0·02		0·31		..	...	0·23	...
19	97·55	..	..	0·43	1·01	.	0·48	..	...	water 0·30	0·23	...
20	99·73	trace	trace	...	0·27		...	...	...	...	...	...
21	98·[illegible]	0·24	0·53	...	0·99	..		...	...	...	...	...
22	98·12	0·24	0·04	..	0·35	...	..	...	.	...	...	...
23	64·75	0·23	...	...	..		..	...	...	...	...	35·02
24	90·55	...	...	...	0·45		.	9·0	...	...	...	...
25	93·12	...	...	...	2·73		..	2·09	0·62	water 1·46	...	...

1, From Vic (Berthier); 2, according to Dufresnoy; 3, from Cheshire (Henry); 4, from Erfurt (Söchting); 5, from Catalonia (Söchting); 6, from Sosnica, near Gleiwitz (Sonnenschein); 7 to 9, from Wilhelmsglück, near Schwabischhall (Fehling); 10, from Stassfurt (Fehling); 11, white rock-salt, from Wieliczka (G. Bischoff); 12, ditto from Berchtesgaden (the same); 13, yellow from Berchtesgaden (the same); 14, from Hall in Tirol (the same); 15, decrepitating salt from Hallstadt (the same); 16, from Schwabischhall (the same); 17, from Stassfurt (Heine and Grund); 18, from Norwich (Dufresnoy); 19, from Stassfurt (Rammelsberg); 20, ditto (Schone); 21, ditto (Benemann); 22, ditto (Scholz); 23, ditto (Tieftrunck); 24, from Saltville, near Abingdon, U.S. (Stieren); 25, from Dieuze (Scheurer-Kestner).

the Dead Sea (with 10·36 per cent. NaCl), and some of the bays of the Caspian. Some analyses of the water of salt lakes are found in Muspratt-Bunte, vi., p. 453.

Further Analyses of Rock-salt.

	France.			Algeria.		Spain.
	Varange-ville	Vic, half-grey	Vic, grey	Uled-kebbad.	Kobbah.	Cardona.
NaCl . .	93·84	97·80	90·30	95·84	72·16	97·87
$MgCl_2$ . .	0·09	...	...	0·53	5·57	0·14
$CaCl_2$ . .	0·05	...	5·00	0·90	1·65	0·14
$MgSO_4$.	...	..	...	...	2·06	...
$CaSO_4$ . .	3·07	0·30	...	...	10·72	0·88
K_2SO_4 . .	...	...	2·00	..	...	...
$CaCO_3$ . .	...	...	...	...	3·71	...
$MgCO_3$.	...	...	.	...	2·89	...
Clay . .	...	1·90	.	.	...	...
SiO_2 . .	...	...		0·33	...	...
Insoluble .	2·74	...	.	...	1·74	0·85
Water . .	0·20	..	0·70	2·40	...	0·12

Analyses of Stassfurt Rock-salt (from Pfeiffer, *Kali-Industrie*, 1887, p. 27).

	1	2.	3.	4.
NaCl . . .	97·55	91·13	99·522	98·020
$MgCl_2$.	...	0·97	...	0·138
Na_2SO_4 . .	0·43	...	...	...
K_2SO_4 . .	...	1·42	0·120	0·305
$MgSO_4$ . .	0·23	0·69	0·185	0·237
$CaSO_4$ . .	1·49	5·44	0·007	0·888
H_2O . . .	0·30	0·35	0·086	0·412

1, Pure transparent (Rammelsberg); 2, opaque salt from underneath a "year-ring" (Pfeiffer); 3, from the upper beds, picked, granular (Precht); 4, the same, medium quality (Precht).

An interesting lake is that at Arzew (province of Oran), which dries up in summer. It has a surface of 8625 acres, and is said to contain 2½ million tons of salt; it is worked for this by the Société Malétra at Rouen.

From the salt lakes in the Astrachan district 100,000 tons of salt are obtained per annum, containing from 87 to 99 per cent. NaCl, 0 to 9 per cent. Na_2SO_4, 0 to 1·7 per cent. $CaSO_4$, 0 to 2·8 per cent. $MgCl_2$, 0·5 to 4 per cent. H_2O, and 0 to 2·5 per cent. insoluble.

The manufacture of common salt from brine (*pan-salt*) is an important industry. Details will be found in a description of the English methods of manufacturing common salt by T. W. Stuart.[1] In America and on the European continent more complicated methods, such as steam-heated and even vacuum pans, are frequently used. Very important improvements in the processes of manufacturing common salt from brine are claimed in the United States patents of Herman Frasch, Nos. 874906 and 874907, of 1907.

Apart from natural brine-springs, salt-wells are artificially produced by bringing the subsoil-water or a weak brine into contact with subterranean rock-salt or salt-clay, and pumping up the strong brine thus formed, in order to boil it down. This is more particularly done in Cheshire, where the greatest salt-making industry of the world is carried on, and where most of the rock-salt is too much contaminated with ferric oxide to be used without purification. Moreover, the coal required for boiling down is very cheap in that locality.

Composition of Natural Salt.

In Muspratt-Bunte, vi., pp. 623-26, a number of tables is given, showing the composition of the various descriptions of salt made from brine in Germany; also of the impure by-products obtained in that industry and of the mother-liquors. The table on p. 16 shows the composition of some kinds of salt produced in England, America, and Belgium.

The suitability of various forms of salt (rock-salt and pan-salt) for the manufacture of saltcake will be treated in Chapter IV.

Brine as such is used in enormous quantities in the manufacture of soda by the ammonia process, and for the manufacture of caustic soda by the electrolytic process, and will be treated in the volumes dealing with these industries.

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[1] *J. Soc. Chem. Ind.*, 1888, p. 660.

Analyses of Common Salt.

	Cheshire common salt, stored.	Spencer, New York.	Pomeroy, Ohio.	Cheshire salt (Brown).	Belgian salt in 1855. (*Rapport sur les Fabriques de Produits Chimiques, p. 56.*)			
					Risle.	Floreffe.	Moustier.	Auvelais.
Sodium chloride	98·250	96·29	93·83	93·16	85·28	88·34	89·89	88·14
Potassium chloride	.	trace	trace	trace	.		...	...
Calcium chloride	0·025	trace	0·89		.	...	..	
Magnesium chloride	0·075	0·27	0·51	0·11	0·18	0·12	0·10	0·16
Sodium sulphate		trace			...	.	..	...
Potassium sulphate		...					..	...
Calcium sulphate	1·550	1·39		1·01	1·67	2·06	1·03	1·18
Magnesium sulphate		...		0·13	0·98	0·67	0·64	0·76
Sodium silicate		0·01	trace			..	.	...
Sodium nitrate		...		...	..	..	...	...
Calcium carbonate		.	.	0·15			..	...
Ferric oxide		0·08	trace	.	.	..	..	...
Alumina		0·17	trace			..	...	...
Insoluble		0·03	trace		0·44	0·36	0·30	0·34
Organic substances		trace	trace		...	...	...	...
Moisture		2·20	4·60	5·44	11·45	8·45	8·04	9·42
	99·900	100·44	99·83	100·00	100·00	100·00	100·00	100·00

Preparation of Pure Salt.

A good deal of stir was made by the "Tee" process, for which Tee and Perkes obtained the Ger. P. 171714, and Tee alone the B. P. 6611, of 1905, the Ger. P. 206569, and the Fr. P. 364731. Pure salt was to be obtained from rock-salt by fusing the latter and treating it with a mixture of steam, air, carbon dioxide and monoxide, some solid fuel being also added. The fused salt was run off, together with the scoria formed. According to *Chem. Trade J.*, vol. xliii., p 562 (19th December 1908), "The International Salt Company" was founded for the purpose of carrying out the invention, the advantages of which are somewhat severely criticised in the same number, p. 559.

The New Salt Syndicate, Limited, obtained a B. P., No. 12110, of 1907, on mechanical contrivances for stirring liquid salt in the process of purification (Ger. P. 204444).

Lawton (B. P. 3866, of 1900) prepares pure salt by volatilising common salt on a hearth heated by gaseous fuel, and condensing the vapours in a cooled chamber.

Taylor[1] contends that absolutely pure salt cannot possibly be obtained on anything like a commercial scale, since it must always take up impurities from the vessels, whether metallic or earthenware, but comparatively less than in other cases from "specially enamelled" cast-iron.

Sodium chloride as a by-product is obtained in various industries, always more or less contaminated with impurities, and is locally employed for making saltcake, but is frequently not very suitable for this purpose. This is, for instance, the case with *kelp-salt*—that is, the salt obtained as a by-product in working Scottish kelp for potassium salts and iodine. It contains about 90 per cent. NaCl, with about 8 per cent. K_2CO_3 and Na_2CO_3. The latter salts give it a certain value for purposes where the alkaline carbonates are employed as such—for instance, for reducing high-strength soda-ash to a lower strength; but in the manufacture of saltcake they are less valuable than NaCl, as they yield no HCl.

The *saltpetre-salt*, which is obtained when converting sodium nitrate by potassium chloride into potassium nitrate, contains about 0·5 per cent. alkaline nitrates, and is not very suitable for making saltcake, as part of the HCl is destroyed, with formation of free chlorine, and the iron pans are very much acted upon.

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[1] *J. Amer. Chem. Soc.*, 1908, xxx., 1631.

Denaturation of Common Salt.

In those countries where common salt is subject to a high duty or to a State monopoly, the manufacture of saltcake would be simply impossible, if a way out of this difficulty was not found in "denaturation." In Great Britain, where previous to 1828 a high duty was laid upon salt and the denaturating process was unknown, the saltcake and soda manufacture, invented forty years before, could not be carried out at all. According to Mactear,[1] the price of salt in Scotland in 1798 was about £3, 10s. per ton, to which £3 was added for duty; and in the same year the duty was raised by £13, so that the price of salt rose to £19, 10s. per ton. In 1805 the duty in Scotland was £12, in England £30 per ton! In 1829, after the duty had been abolished, the price of salt in Scotland fell to £1, 2s. per ton, and this immediately called into existence the great alkali industry. Later on the price of salt in Scotland and on the Tyne sank to about 15s., in Lancashire to about 6s. per ton, and in Cheshire, in the shape of brine pumped over ground, inclusive of royalty, the price of salt is only 6d. per ton.

In Germany the duty on salt is still in existence, and would be much too high to permit of decomposing the salt for saltcake, but the duty is avoided by "denaturating" the salt under official supervision. The substances mixed with salt for this purpose are very different. *Fischer's Jahresber.*, 1886, p. 277, enumerates:—4 to 15 per cent. soda-ash; 12 per cent. soda crystals; 2 per cent. sulphuric acid 148° Tw.; 2 per cent. strong hydrochloric acid; 10 per cent. bicarbonate of soda; liquor ammoniæ; a solution of aniline colours; 5 to 16·66 per cent. Glauber's salt. Evidently for salt intended for the saltcake manufacture the best denaturants are sulphuric acid, sulphate of soda, and nitre-cake. Of course it must be analysed and a certain proportion of sulphuric acid, corresponding to the

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[1] *Report on the Alkali and Bleaching Powder Manufacture of the Glasgow District*, p. 4.

"free acid" in the nitre-cake, must be deducted from the charge in the saltcake pan. Nitre-cake ought not to be mixed with the salt in pieces, but in the crushed state (see later on).

In large works it pays better to have the decomposition of salt checked by a regular staff of Excise officers rather than incur the expense of denaturing.

Statistics.

The following figures referring to the production of salt in Great Britain in former years will still present some interest:—

Production of Salt in Great Britain.

Period	Average per year	Duty per ton.	Price per ton
	Tons	Shillings	Shillings.
1800 to 1806	203,000	600	640
1807 " 1815	230,000	600	640
1816 " 1823	257,000	600	640
1824 " 1840	410,000		20
1841 " 1860	880,000		16
1861 " 1870	1,540,000		14
1871 " 1880	2,020,000		12
1881	2,558,368		...
1882	2,645,000		...
1883	2,298,220	...	...
1884	2,332,704	...	...
1885	2,207,683	...	...
1886	2,142,220	...	...
1887	2,193,951	...	...
1888	2,305,569		
1889	1,946,496		...
1890	2,146,849		

The following statements on the production of salt in the whole world since the year 1890 have been compiled from the various volumes of *The Mineral Industry*, edited by Rothwell and later on by Ingalls. The unit employed there is the metric ton = 0·9842 English long tons = 1·1023 American short tons. We have abridged this to kilo-tons, representing 984·2 English or 1102·3 American short tons each. The figures for the United States for the years 1906 and 1907 are calculated from the official reports of the U.S. Geological Survey:—

Year.	Algeria.	Austria.	Canada.	France.	Germany.[1]	Greece.	Hungary.	India.	Italy.[2]	Japan.	Russia.	Spain.	United Kingdom.[3]	United States.
1890	24	304	40	843	1050	18	160	1053	27		1388	615	2182	1113
1891	35	391	41	811	1170	20	163	1032	41		1351	583	2077	1300
1892	13	288	41	974	1167	22	180	916	24		1400	683	1988	1497
893	19	306	57	1114	1168	78	157	853	25		1351	361	2015	1478
894	18	312	52	891	1253	21	169	1318	31		1354	520	2272	1498
895	26	279	48	871	1212	22	169	1121	29		1540	326	2208	1813
896	20	309	40	1043	1303	23	180	1043	29		1347	522	2055	1995
897	23	331	47	948	1307	20	172	938	32	622	1552	509	1934	2010
898	21	342	52	999	1370	25	179	1046	30	647	1506	479	1909	2382
899	17	342	52	1194	1432	37	185	977	29	599	1681	598	1946	2523
900	18	330	56	[illegible]	1514	22	189	1021	367	670	1968	450	1874	2651
901	19	333	54	910	1564	24	187	1120	435	659	1706	345	1812	2612
902	27	311	57	864	1583	25	172	1057	458	621	1847	426	1924	2409
903	26	359	57	968	1694	25	183	909	488	657	...	427	1917	2409
904	19	370	62	1154	1702	27	188	1189	464	.	.	544	1922	2797
905	27	343	41	1130	1778	..	195	1425	438	...		552	1920	3297
906	...		69		1868	...	...	..	.		..	..	1985[4]	3578
907	...	...	..		1951		..	...	...			...	...	3773

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[1] In Germany the brine consumed for the manufacture of ammonia soda is not included in those returns.

[2] For the years 1890 to 1899 only rock and brine salt; from 1900 also sea-salt (Italy).

[3] The figures for the United Kingdom include the salt contained in brine sent to alkali works.

[4] From *Chem. Trade J.*, vol. xliii., p. 448. Comprises 246,020 tons rock-salt from brine, and 1,738,636 salt produced from brine or ntained in brine sent to alkali works.

In 1908 the quantity of salt produced in the United States[1] was 28,822,062 barrels of 280 pounds, valued at $7,553,632; in 1907 the production reported was 29,704,128 barrels, valued at $7,608,323. Expressed on a tonnage basis, these quantities represent an output of 4,158,578 short tons in 1907 and of 4,035,089 short tons in 1908. In 1907 the average net value was 25·614 cents per barrel, or $1·83 per short ton; and in 1908, 26·208 cents per barrel, or $1·87 per short ton.

The following table shows the quantity and value of salt reported as produced in the United States from 1900 to 1908:—

	Barrels.	Value.
1901 . .	20,566,661	$6,617,449
1902 . . .	23,849,231	5,668,636
1903 . .	18,968,089	5,286,988
1904 . .	22,030,002	6,021,222
1905 . .	25,966,122	6,095,922
1906 .	28,172,380	6,658,350
1907 . . .	29,704,128	7,608,323
1908 . . .	28,822,062	7,553,632

Salt consumed for the Manufacture of Saltcake and Soda.

The statements concerning the quantities of salt *consumed* in Great Britain and Ireland *for the manufacture of saltcake and soda*, up to the year 1877, rest on somewhat uncertain data; from that year we have the annual Reports of the Alkali Makers' Association. The following table is taken from E. K. Muspratt's paper in the *J. Soc. Chem. Ind.*, 1886, p. 412, up to the year 1884; from 1885 to 1896 we have compiled from the official reports of the inspectors under the Alkali Act. The brine consumed in the manufacture of ammonia soda is taken into account, assuming 1·46 tons of salt consumed for each ton of ammonia soda manufactured. The salt consumed in the wet copper-extraction process is not reckoned from 1885 onwards. From 1897 onwards these statistics are not found in the official reports.

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[1] *U.S. Geol. Survey*, 1909.

Year.	Consumed for Saltcake and Leblanc soda	Consumed for Ammonia soda.	Consumed for Wet Copper-extraction.	Total.
	Tons	Tons.	Tons.	Tons.
1852	...	...	...	137,547
1860	...	...	...	250,000
1861	...	...	...	235,360
1862	...	...	...	254,600
1866	...	...	.	351,000
1869	...	...	...	306,905
1871	...	...	..	352,350
1874	...	...	...	459,756
1876	...	...	...	538,600
1877	552,570	9,082	16,549	578,201
1878	535,154	16,230	17,158	568,542
1879	575,447	22,669	17,171	615,287
1880	648,587	27,416	24,013	700,016
1881	620,064	29,783	25,252	675,099
1882	598,833	56,914	24,188	679,935
1883	602,921	77,015	25,796	705,732
1884	578,874	89,759	21,869	690,502
1885	598,096	115,032	.	713,128
1886	584,323	137,220	...	721,543
1887	577,381	158,636	...	736,017
1888	590,312	212,181	...	802,493
1889	584,203	219,279	...	803,482
1890	602,769	252,260	...	855,029
1891	567,863	278,528	...	846,391
1892	519,593	304,897	..	824,490
1893	467,562	349,609	...	817,171
1894	434,298	361,603	..	795,901
1895	408,173	428,614	...	836,787
1896	360,929	431,577	...	792,506

II. SULPHATE OF SODA.

Normal sodium sulphate, Na_2SO_4, is one of the principal products of the alkali industry; it is also found in nature in large quantities. As a technical product it is, in the anhydrous state, generally styled "saltcake," and in the decahydrated state "Glauber's salt."

Before the ammonia soda and electrolytic processes entered so much into competition with the Leblanc process, the manufacture of saltcake was much more important than at present. Nowadays, natural sulphate, and Glauber's salt obtained as a by-product in various cases also compete with the manufactured saltcake. Nevertheless this manufacture is still a most important branch of industry, both for Leblanc soda and for glass-making; and a large quantity of saltcake is also manufactured to obtain hydrochloric acid as a principal product.

Historical Notes.[1]—Sodium sulphate was first described by Glauber, in his treatise *De Natura Salium* (1658). He made it from the residue remaining after the preparation of hydrochloric acid from common salt and sulphuric acid, and gave it the name *sal mirabile*, strongly recommending it for internal and external use; later on it was called, after himself, *sal mirabile Glauberi*. Kunkel, however, in his *Laboratorium Chymicum* (1716), asserts that Glauber's salt had been known as an arcanum to the Electoral house of Saxony a century before Glauber. On a large scale it was first produced from salt-brine at Friedrichshall in Hildburghausen, and has been known since 1767 as *sal aperitivum Fridericianum* or *Friedrichssalz*. At that time it was obtained by freezing-out on cold winter-nights (see below).

Anhydrous sodium sulphate, Na_2SO_4 (Na = 32·38 per cent.; SO_4 = 67·62 per cent.). This salt, which is found in nature as the mineral *Thenardite*, is obtained in the pure state by dehydrating crystallised Glauber's salt, or by crystallising from solutions above 33°, or from strongly alkaline solutions at the ordinary temperature. The "saltcake" of commerce is impure sodium sulphate. It crystallises in the rhombic system with an octahedral habit; its density is 2·655 (at the fusing-point 2·104).

Melting-point is variously given as follows:—

Carnelley (1878) = 861° ± 3°; Meyer, Riddle, and Lamb (1893) = 863·2°; Le Chatelier (1887) = 867°; M'Crae (1895) = 881·5°, 885·2°; Heycock and Neville (1895) = 883·2°; Ramsay and Eumorfopulos (1896) = 884°; Ruff and Plato (1903) = 880°. At a white heat it volatilises, and boils at "about the temperature of melting iron." This indicates that the boiling-point lies between 1000° and 1600°, and there appears to be no more definite information available at present than this vague statement. The residue from the incomplete evaporation of sodium sulphate has an alkaline reaction.

Specific heat of sodium sulphate is given by Schüller as 0·2293 (28° to 57°), and of fused sodium sulphate (17° to 98°) by Regnault as 0·2312.

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[1] *Cf.* Kopp, *Geschichte der Chemie*, iv., p. 40.

Density of anhydrous sodium sulphate at 15° is 2·673. For the melted salt, Brunner gives:

$$d_t = 2.065 - 0.00045\,(t^\circ - 900^\circ).$$

Modifications of Sodium Sulphate.—According to Coppet,[1] two modifications of sodium sulphate exist:—*a*, formed by the efflorescence of the hydrated salt at ordinary temperature, and *β*, formed by heating above 33°. Only the *a* modification is capable of causing crystallisation of a supersaturated solution.

Pickering[2] also gives evidence of the existence of two modifications. He states that the heat of solution of the salt, dehydrated at 150° or obtained anhydrous by boiling the aqueous solution, is 57 calories; that of the salt ignited at a red heat, 760 calories; and that of the fused salt, 857 calories. After keeping for three months, the heat of solution of fused salt was found to have fallen to 438 calories.

Thomsen gives the heat of solution of fused sodium sulphate (in 400 mols. of water) as 460 calories; that of the anhydrous effloresced salt as 170 calories (that of the decahydrate is negative).

Heat of Formation.—The heat of formation at 15° from the elements is 327,000 calories. The heat of neutralisation of 1 mol. of sulphuric acid by 2 mols. of sodium hydroxide, each dissolved in 4 litres of water, is 317,000 calories at 15°.

The heat of formation in solution of $NaHSO_4$ from 1 mol. of H_2SO_4 and 1 mol. of NaOH is 14,600 calories.

Hydrates of Sodium Sulphate.

The existence of the *monohydrated sodium sulphate* which is said to separate at 30° when a saturated solution is warmed, is very doubtful.

A *dihydrated sodium sulphate* has been described by Thomsen, but the existence of this hydrate is extremely doubtful.

Heptahydrated sodium sulphate often separates on cooling a solution which has been saturated at temperatures above 33°. It is unstable over the whole range of its existence, and the crystals in the air rapidly become dull through conversion into a mixture of anhydrous salt and the decahydrate.

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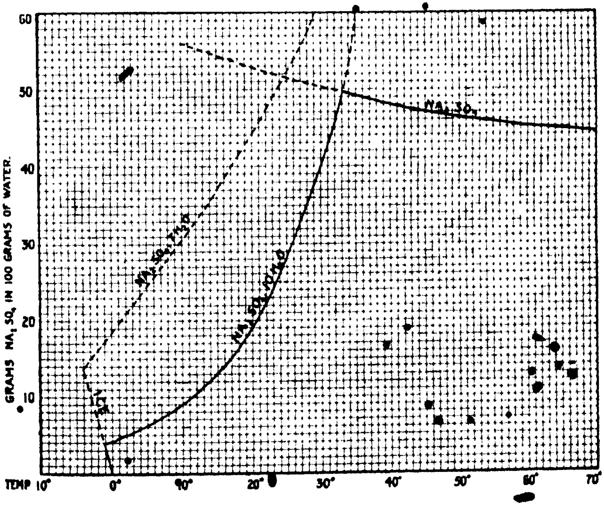
[1] *Comptes rend.*, 87, 194.

[2] *J. Chem. Soc.*, 1884, 686.

For a recent investigation of this change, see D. Gerney.[1]

Sodium sulphate decahydrate, Na_2SO_4, $10H_2O$, or *Glauber's salt*, is an important article of commerce. It separates from solutions below 33° or on evaporation of solutions at ordinary temperatures. The transition temperature of pure Na_2SO_4, $10H_2O$ is, according to E. von Biron and S. P. Malschevsky,[2] 32·45°. The same investigators show the changes produced in the transition temperature and in the solubility by the presence in various amounts of sodium chloride, sodium bromide, sodium iodide, sodium chromate, dextrose, and alcohol. Solubility determinations at the transition temperature gave results for the pure salt averaging 49·59 g. of anhydrous Na_2SO_4 per 100 g. of water.



C. Leenhart and A. Bontarie[3] give the latent heat of fusion of the decahydrate at 31·3° = 56·9 which gives K = 32·5 in van t'Hoff's formula, agreeing well with the experimental figure.

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[1] *Comptes rend.*, 1909, **149**, 77.

[2] *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1619.

[3] *J.U.S. Abs.*, 1913, p. 669.

The boiling-point of a saturated solution of sodium sulphate is about 103·2°.

The following table shows the solubility of sodium sulphate and its hydrates:—

Solubility of Sodium Sulphate in Water.

Temp. °C.	Salt separated at the bottom.	Grms. Na_2SO_4 dissolved in 100 grms. water.	Observer.
0	$Na_2SO_4, 10H_2O$ . .	5·0	Loewel.
+10	" " . .	9·0	"
15	" " . .	13·2	"
20	" " . .	19·4	"
25	" " . .	28·0	"
30	" " . .	40·0	"
34	" " . .	55·0	"
fus.-pt. 34	" " . .	78·89	Tilden and Shenstone.
−8·55	Ice + $Na_2SO_4, 7H_2O$ . .	14·5	De Coppet.
0	$Na_2SO_4, 7H_2O$ . .	19·6	Loewel.
+10	" " . .	30·5	"
20	" " . .	44·7	"
26	" " . .	55·0	"
+18	Na_2SO_4	53·3	"
20	"	52·8	"
24·4	$Na_2SO_4, 7H_2O$ . .	51·8	"
25	Na_2SO_4	51·5	"
30	"	50·4	"
32·88	$Na_2SO_4, 10H_2O$ . .	...	Richards and Wells.
32·5	" " . .	49·6	Interpolated from Gay-Lussac's results.
35	Na_2SO_4 rhombic crystals.	49·4	" "
40	" " .	48·2	" "
50	" " .	46·8	" "
60	" " .	45·5	" "
70	" " .	44[illegible]	" "
80	" " .	43·7	" "
90	" " .	42·9	" "
100	" " .	42·7	" "
101·9	" " .	42·2	Berkeley, at 751 mm. pressure.
120	" " .	41·9	Tilden and Shenstone.
140	" " .	42·0	"
160	" " .	42·9	"
180	" " .	44·2	"
230	" " .	46·4	"
150	" " .	42·2	Etard.
190	" " .	42·7	"
240	" " .	42·9	"
320	" " .	21·7	"

The solubility of sodium sulphate and its hydrates are also shown graphically in the diagram on p. 25. It will be noted that the solubility of the anhydrous salt diminishes with increasing temperature. The heptahydrate is unstable at all temperatures but its solubility has been measured by Loewel.

Specific Gravity of the Solutions of Sulphate of Soda at different Degrees of Concentration at 15° C., according to Gerlach.

Per cent.	Na_2SO_4.	Na_2SO_4, $10H_2O$.	Per cent.	Na_2SO_4.	Na_2SO_4, $10H_2O$.
1	1·0091	1·004	16	..	1·064
2	1·0182	1·008	17	..	1·069
3	1·0274	1·013	18	..	1·073
4	1·0365	1·016	19	...	1·077
5	1·0457	1·020	20	..	1·082
6	1·0550	1·024	21	.	1·086
7	1·0644	1·028	22	..	1·090
8	1·0737	1·032	23	.	1·094
9	1·0832	1·036	24	..	1·098
10	1·0927	1·040	25	.	1·103
11	1·1025	1·044	26	...	1·107
12		1·047	27	...	1·111
13	.	1·052	28	...	1·116
14	..	1·056	29	...	1·120
15	.	1·060	30	...	1·125

At 19°, according to Schiff[1]:—

Spec. grav.	Per cent. Na_2SO_4, $10H_2O$.	Per cent. Na_2SO_4.	Spec. grav.	Per cent. Na_2SO_4, $10H_2O$.	Per cent. Na_2SO_4.
1·0040	1	0·441	1·0642	16	7·056
1·0079	2	0·882	1·0683	17	7·497
1·0118	3	1·323	1·0725	18	7·938
1·0158	4	1·764	1·0766	19	8·379
1·0198	5	2·205	1·0807	20	8·820
1·0238	6	2·640	1·0849	21	9·261
1·0278	7	3·087	1·0890	22	9·702
1·0318	8	3·528	1·0931	23	10·143
1·0358	9	3·969	1·0973	24	10·584
1·0398	10	4·410	1·1015	25	11·025
1·0439	11	4·851	1·1057	26	11·466
1·0479	12	5·292	1·1100	27	11·907
1·0520	13	5·733	1·1142	28	12·348
1·0560	14	6·174	1·1184	29	12·789
1·0601	15	6·615	1·1226	30	13·230

Sodium sulphate is not appreciably soluble in absolute alcohol at ordinary temperatures, a little more so in alcohol acidulated with sulphuric acid. Therefore alcohol precipitates sodium sulphate from a cold saturated solution. In dilute alcohol it is more soluble; the saturated solution, according to Schiff,[1] contains at 15° C.:—

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[1] *Ann. Chem. Pharm.*, cx., p. 70.

Alcohol of spec. grav.	Per cent. C_2H_6O by weight.	Per cent. of $Na_2SO_4+10H_2O$.
1·000 (water)	0	25·6
0·976	10	14·35
0·972	20	5·6
0·939	40	1·3

It is soluble in glycerine, less so in strong acetic acid, soluble in hydrochloric acid with strong evolution of heat. In some saline solutions it is more easily soluble than in pure water—for instance, in solutions of potassium sulphate, magnesium sulphate, potassium chloride, and potassium nitrate. The increased solubility in these cases is due probably to the formation of complex salts. On pounding together sal-ammoniac and Glauber's salt, the dry mixture becomes damp, the temperature being lowered at the same time, and a mixture of ammonium sulphate, sodium chloride, and water is formed, of which the last previously existed in the crystals.

Chemical Reactions of Sodium Sulphate.

A current of hydrochloric acid gas at a red heat converts sodium sulphate entirely into sodium chloride, sulphuric acid being set free: we shall discuss this more in detail when describing the properties of hydrochloric acid. This process takes place in progressive stages.[2] When sodium sulphate is ignited with calcium carbonate there is no decomposition (Scheurer-Kestner and Kolb), which is of importance for the theory of the soda-process. A mixture of Na_2SO_4 with Al_2O_3 is not changed even on prolonged heating to redness, but in the presence of water and coal, sodium aluminate is formed. Fused with silica and coal, it yields silicate of soda; on fusion with iron and caustic soda, Fe_3O_4 and the sulphates f iron and sodium are formed. Its solution is decomposed ery incompletely by milk-of-lime into calcium sulphate and austic soda; but, according to Tessié du Motay,[1] at a pressure f 2 to 20 atmos. 75 to 80 per cent. of the sodium sulphate is austicised by lime.

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[1] *Ann. Chem. Pharm.*, cxviii., p. 365.

[2] Colson, *Comptes rend.*, cxxiii., p. 1285.

When an intimate mixture of Na_2SO_4 and animal charcoal s heated in an iron pipe,[2] no interaction takes place below 950°, ut at this temperature the reduction is rapid and uniform, specially if carbon is used in the proportion required by the quation:

$$Na_2SO_4 + 4C = Na_2S + 4CO.$$

With this mixture, 70 per cent. of the sulphate is decomposed n twenty minutes. With increase of temperature, the rate of eaction increases rapidly.

J. W. Cobb[3] found that in dry air sodium sulphate commenced to decompose, as evidenced by the evolution of sulphur ases at 1200° to 1220° and dissociated more rapidly at 1330° to 1350°.

In dry hydrogen decomposition, as shown by evolution of ulphuretted hydrogen, commenced at 530° to 540°, increasing teadily with the rise in temperature to fairly free decomposition t 900°. No decomposition could be counted as due to silica r alumina if the atmosphere was reducing.

Acid Sodium Sulphates.

1. *Trisodium hydrogen disulphate*, $Na_3H(SO_4)_2$, described by Thomsen and Mitscherlich on very flimsy evidence, has been solated and its existence definitely proved by Butler and Dunnicliff.[4]

2. *Acid sodium sulphate or sodium bisulphate*, $NaHSO_4$, is eadily formed by heating common salt with two equivalents f sulphuric acid. From a hot solution it crystallises as the nhydrous salt and from a cold solution as the monohydrate.

(*a*) The *anhydrous crystals* are transparent, long, quadrilateral prisms with oblique end faces. They remain brilliant on drying, but the surface becomes dull on exposure to the air although the crystals do not deliquesce. Sp. gr. 1·8; melting-point 149°. Heated above the melting-point, the salt decomposes, yielding the pyrosulphate:

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[1] *Ber.*, v., p. 741.

[2] A. Colson, *Comptes rend.*, 1909, **149**, 1076.

[3] *J. Soc. Chem. Ind.*, 1910, **29**, 72 and 399.

[4] *Trans. Chem. Soc.*, 1920, **117**, 649.

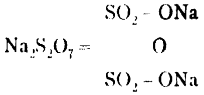
$$2NaHSO_4 = Na_2S_2O_7 + H_2O.$$

Water decomposes the salt partly into the normal sulphate and free acid. For the action of anhydrous alcohol on the salt, see Butler and Dunnicliff.[1]

(*b*) The *monohydrate*, $NaHSO_4, H_2O$, forms large transparent crystals of the monoclinic system.

3. *Monosodium Trihydrogen Disulphate*.—For information as to the existence of this and other acid sodium sulphates, reference may be made to Kendall and Landon.[2]

4. *Sodium pyrosulphate*,



$$Na_2S_2O_7 = \begin{matrix} SO_2-ONa \\ O \\ SO_2-ONa \end{matrix}$$

remains behind on heating sodium chloride with sulphuric anhydride:

$$2NaCl + 4SO_3 = Na_2S_2O_7 + S_2O_5Cl_2,$$

and on igniting the acid sulphate (*cf.* No. 2); it also separates along with the latter from a solution of sulphate in fuming oil of vitriol; it may also be precipitated from the fuming oil of vitriol of trade (in which it occasionally occurs) by means of boiling nitric acid, aqua regia, chlorine, ether, or alcohol. It probably also occurs in ordinary furnaced saltcake. Exposed to a bright red heat, it splits up into neutral sulphate and sulphuric anhydride, according to the equation $Na_2S_2O_7 = Na_2SO_4 + SO_3$; this is the cause, at least partly, of the thick white vapours which hot calcined saltcake emits on being drawn out of the furnace.

P. Pascal[3] has studied the system sodium sulphate-sulphuric acid-water, at temperatures between −45° and 210° C., defining the conditions of existence in contact with solution of the following solid phases:—Ice, Na_2SO_4; $Na_2SO_4, 10H_2O$, Na_2SO_4,

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[1] *Trans. Chem. Soc.*, 1920, **117**, 649.

[2] *J. Amer. Chem. Soc.*, 1920, **42**, 2131.

[3] *Comptes rend.*, 1917, **164**, 628-630.

$NaHSO_4$; $NaHSO_4, H_2O$; $NaHSO_4, NaHSO_4, H_2SO_4, 1{\cdot}5\ H_2O$, and $NaHSO_4, H_2SO_4$. The conditions of existence of the hydrate, $Na_2SO_4, 7H_2O$, are less clearly defined, whilst some evidence was obtained of the existence of the compounds $Na_2SO_4, 2NaHSO_4$ and $H_2SO_4, 2NaHSO_4$. From the data afforded by his diagram, the author proceeds to the discussion of the results of cooling nitre-cake, and of crystallising solutions of bisulphate in water. By pouring fused nitre-cake into water and allowing to cool so that crystals of $NaHSO_4$, Na_2SO_4 separate, it would be possible to obtain a mother-liquor richer in free acid and with a relatively low content of normal sulphate. The acid sulphates and pyrosulphate of sodium have been examined by J. D'Ans,[1] who determined the solubility isotherm of the system $SO_3—H_2O—Na_2SO_4$ at 25°, with the following solid phases in contact with the solution:—$NaHSO_4$, $NaH_3(SO_4)_2, H_2O$; $Na_2SO_4, 4{\cdot}5\ H_2SO_4$; $NaHS_2O_7$. D'Ans gives also data and triangular diagrams for ternary system $SO_3—H_2O—Na_2O$ at 25°.

The properties and composition of *commercial salt-cake* will be described in a later chapter. The *nitre-cake* of commerce is a mixture of normal and acid sodium sulphate in varying proportions, obtained as a by-product in the manufacture of nitric acid.[2]

Natural Occurrence of Sodium Sulphate.

Sodium sulphate is found in nature both in the anhydrous state as *thenardite* and as the decahydrate (*mirabilite*). It occurs in combination with calcium sulphate (as *glauberite*), as a constituent of natural soda, dissolved in mineral waters, sea-water, etc. In some places Glauber's salt is obtained from these sources on an industrial scale.

Thenardite (Na_2SO_4) crystallises rhombically, in pretty large pointed pyramids combined into crusts; its surface is rough, its taste faintly saline. In the air it becomes dull by absorbing water. Its principal occurrence is in the rock-salt beds at Espartinas, near Aranjuez, also in Peru (Tarapaca, etc.).

In combination with water, sodium sulphate occurs in several species of minerals; with 10 mols. of water as *mirabilite*, mostly only as efflorescences and crusts on rocks or old walls, but in larger quantities at Mühlingen, in the Aargau, in gypsum, in the salt beds at Hallstadt and Aussee. Other species, containing magnesia, are *reussin*, *loeweite*, and *bloedite* (from Ischl).

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[1] *Z. anorg. Chem.*, 1913, 80, 235.

[2] *Cf.* Nitric Acid volume.

In the Ebro valley, especially near Lodosa, some years ago large beds of hydrated sodium sulphate were found, as glassy layers from about 2 feet up to several yards in thickness, between beds of clay and gypsum. Similar beds have been found at Calatayud and Corvora, in Catalonia, near Santander, in Old Castile, and other places. These beds are principally worked at Lodosa, Alcanadra, and Andosilla, and also at Calmenar de Oreja, in the province of Madrid. This Spanish sulphate is quite free from iron, and is consequently very well adapted for glass-making; but most of the English consumers have given up its use again, owing to its variable quality.

An enormous bed of thenardite, containing 97 per cent. sodium sulphate, was found at Castellar, near Villarubia de Santiago, Toledo, and has been already worked to some extent. It forms a layer 33 feet thick over the rock-salt, and the quantity already proved amounts to 2 million tons. It contains some iron, viz., 0·21 per cent. $Fe_2O_3+Al_2O_3$, but this is usable for ordinary glass.[1]

Other occurrences of more or less hydrated sulphate are:—in Hungary, Switzerland, Italy, France (St Rambert), as *exanthalose* with 20 per cent. water (a volcanic product of Vesuvius), in a cavern at Kailua, on the island of Hawaii; as an efflorescence on the Siberian and Caucasian steppes, on the limestone below the falls of the Genesee, and on the Sweetwater River in the Rocky Mountains.

Analysis of Different Minerals of this kind.

	Mirabilite of St Rambert.
	Per cent.
Na_2O . . .	20·0
MgO . . .	0·7
SO_3 . . .	26·0
HCl . . .	trace
H_2O . . .	53·0

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[1] *J. Soc. Chem. Ind.*, 1899, p. 1167.

	Bloedite (John).	Reussin (Reuss).	Astrakanite from the mouth of the Volga (Gobel).
	Per cent.	Per cent.	Per cent.
Na_2SO_4	33·34	66·04	41·00
$MgSO_4$	36·66	31·35	35·18
$CaSO_4$	...	0·42 (including sand)	1·75
$MnSO_4$	0·33	..	..
$FeSO_4$	0·34	...	..
NaCl	0·33	...	..
$CaCl_2$	...	2·19	...
$MgCl_2$	..	...	0·33
H_2O	22·00	...	21·56

The double sulphate of sodium and calcium, called *glauberite*, is found in quantity, for instance in the salt-mines of Villarubia in Spain, of Vic in France, of Berchtesgaden in Bavaria, of Stassfurt, in the province of Tarapaca, etc. Analyses of it have shown :—

	Varangeville (Pisani).	Villarubia (Brogniart).	Berchtesgaden (Kobell).
	Per cent.	Per cent.	Per cent.
Na_2SO_4	50·50	51	48·6
$CaSO_4$	48·78	49	51·0
Clay	0·40	...	...

	Atacama (Hayes).
	Per cent.
Na_2O	21·32
CaO	20·63
Fe_2O_3	0·14
SO_3	57·22

Lunge quotes the following analyses of *thenardite*, I. and II. from a French works and IV. from Tarapaca. II. is evidently *glauberite*.

	I.	II.	III.	IV.
	Per cent.	Per cent.	Per cent.	Per cent.
Na_2SO_4	97·50	46·77	99·78	97·48
$CaSO_4$	2·06	41·90	..	...
Na_2CO_3	..	..	0·72	..
Al_2O_3	...	0·30	...	.
Fe_2O_3		0·25	..	
H_2O	0·15	5·84	..	
Insoluble (SiO_2, etc.)	.	4·94	.	2·19

In North America very large quantities of thenardite are found, *e.g.*, near the Verde River, Maricopa County, Arizona. Allen and Durham's analysis[1] shows 43·01 Na_2O; 56·35 $SOSO_3$; 0·12 CaO; 0·02 MgO; 0·09 Cl; 0·38 insoluble. *Cf.* later on under "Natural Soda."

Very frequently sodium sulphate is found along with natural soda (trona) and common salt—for instance, in the water of the lakes of the Araxes plain and the salts crystallising out of it, which have been studied especially by Abich.[2] Both on the surface and at the bottom of the lakes such salts are separated almost free from water, in consequence of the mother-liquor being saturated with other salts, especially NaCl. The following analyses show the composition of these salts, as well as of the pink mother-liquor, containing 30·63 per cent. of mineral salts, and of that of some alkaline small pools in the neighbourhood, containing 34·7 per cent. of mineral salts:—

	Salts at the surface	Salts at the bottom.	Mother-liquor salts	Alkaline pools (dry)
	Per cent	Per cent	Per cent	Per cent.
Na_2SO_4	80·56	78·44	18·18	15·55
Na_2CO_3	16·09	18·42	12·08	68·9
NaCl	1·62	1·92	69·73	15·5
H_2O	0·55	1·18	.	...

In the Russian Caucasus, near Batalpachinsk, 16 miles from Barsanky railway-station, there are two lakes, containing solutions of nearly pure sodium sulphate. They have no outlets, and the water coming down during the rainy season evaporates in summer, so that Glauber's salt is formed on the surface; the same salt is formed in winter by the cold, in layers from ½ in. to 7 in. thick. After drying it yields sodium sulphate of 95 per cent. The inhabitants of this district consume hundreds of tons of it. Gauthier calculates the whole contents of the lakes as at least 260,000 tons.[1]

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[1] *Fischer's Jahresber.*, 1882, p. 335.

[2] *J. prakt. Chem.*, xxxviii, p. 4.

The following information on this Caucasian occurrence of sodium sulphate was supplied privately to Dr Lunge. The smaller of these "lakes" (or rather ponds) has a surface of 430 acres and a depth of a little over a foot; the larger a surface of about 2300 acres and the same depth as the other, one side sloping gently. The water contains, if of sp. gr. 1·142, 293·3 g. Na_2SO_4, 10 H_2O, 48·34 g. NaCl and 11·35 g. $MgSO_4$ per litre. The Glauber's salt crystallising from it is very pure; it contains after drying:—

	I	II
	Per cent.	Per cent.
Na_2SO_4	98·82	99·18
NaCl	0·72	0·29
Na_2CO_3	...	0·06
Insoluble	0·31	0·33
H_2O	0·15	0·17

The total stock of crystallised Glauber's salt in those lakes s officially estimated at 655,000 metric tons, of which 400,000 ons is practically obtainable.

During the months of June, July, and August the water s pumped into four large tanks, made in the clay, 430 ft. ong, 260 ft. wide, and 8 ft. deep, and it is left there for two ears. In summer it is concentrated by spontaneous evaporaion, and in winter Glauber's salt crystallises out. Each of he four tanks in the two years produces about 4750 tons f Glauber's salt. Attempts at dehydrating the salt by heating n iron pans and calcining gave very unsatisfactory results. pon Lunge's advice the salt was exposed in open sheds during he summer heat, and by efflorescence yielded an almost nhydrous product, perfectly free from iron and containing 8·53 per cent. N_2SO_4, with 0·59 NaCl, immediately fit for late-glass making.

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[1] *Chem. Ind.* 1890, p. 167.

Bachmetjew[1] mentions a bed of very pure Glauber's salt (43 per cent. Na_2SO_4, 55 per cent. H_2O, 2 per cent. impurities), which occurs 20 miles east of Tiflis, 7 ft. below the ground, and has a depth of from 5 to 10 ft.

A considerable quantity of Glauber's salt is formed in the Karabugas Bay, in the Caspian Sea.[2] That bay has a surface of 66 square miles; its depth in the deepest place is only 60 ft. Owing to the strong evaporation, there is a constant flow of water through the strait connecting this bay with the Caspian Sea. The water of this sea contains per litre 0·78 g. NaCl, 0·04 KCl, 0·05 $MgCl_2$, 0·30 $MgSO_4$, 0·08 $CaSO_4$, 0·02 $CaCO_2$, and is of sp. gr. 1·01, but the water in the centre of the bay comes up to 1·18 or 1·19. In the central part of the bay a layer of pure crystallised Glauber's salt, 1 ft. thick, has been formed, the mass of which is estimated to be about 1000 million tons.[3]

Markownikoff[4] gives further notes on native sulphate of soda in Russia.

Zoleski[5] mentions several mountain lakes in Siberia from which sodium sulphate is obtained, and is converted at Barnaul into soda-ash by the Leblanc process.

Paternò[6] describes the occurrence of mirabilite at Bompensieri, near Montedoro, in Sicily, where a 7-ft. deep layer of it is worked for sale. The salt contains 55·68 per cent. water, and on drying 55·15 to 55·25 per cent. SO_3, and is therefore very pure.

Large deposits of sodium sulphate are found in the lowest portion of the Carriso Plain, which extends along and within the north-east boundary of San Luis Obispo County, California.[7] The lake known locally as Soda Lake, or Salt Lake, in the bed of which this salt occurs, receives the drainage from the Carriso Plain and the adjoining flanks of the bounding ranges, the total catchment basin being somewhat over 525 square miles in extent. The lake includes an area of nearly 3000 acres. It remains practically dry except in extraordinarily wet seasons. A sample of the salt collected at the surface of the lake, near the present evaporation plant, varies from dull to lustrous pure white in colour, and, though more or less granular, may be easily crushed between the fingers. An analysis of the salt, made in the laboratory of the U.S. Geological Survey, shows it to contain 40·5 per cent. of sodium oxide (Na_2O), 46·12 per cent. of sulphuric anhydride, 1·66 per cent. of magnesium oxide, and 9·27 per cent. of chlorine.

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[1] *Chem. Zeit.*, 1884, p. 652.

[2] *Fischer's Jahresber.*, 1898, p. 338.

[3] *Cf.* also *Chem. Zeit.*, 1903, p. 1177.

[4] *Fischer's Jahresber.*, 1887, p. 528.

[5] *Chem. Zeit.*, 1893, p. 1695.

[6] *Liebig's Jahresber.*, 1880, p. 1423.

[7] *Oil, Paint, and Drug Rep.*, 31st May 1929.

III. HYDROCHLORIC ACID.

Historical.

The ancients were already acquainted with the cementation of argentiferous gold by heating it with common salt and copperas or alum, in which case hydrochloric acid is set free and comes into action. To the Arabian alchemists aqua regia was well known; but pure aqueous hydrochloric acid is first mentioned by Basilius Valentinus in the fifteenth century. At the end of the sixteenth century Libavius mentions its evolution by heating salt with clay; Glauber in 1648 still calls it the dearest of all acids and the most difficult to prepare! He kept secret its preparation from salt and oil of vitriol, discovered by himself. He also knew hydrochloric acid gas, but Priestley in 1772 first collected this gas over mercury, and described its properties.[1]

Properties of Hydrochloric Acid (Muriatic Acid), HCl.

Hydrochloric acid is sometimes found in nature in the ree state or in aqueous solution—for instance, in volcanic xhalations, springs and brooks, and in the water of some ivers along with free sulphuric acid. In the animal body ydrochloric acid is stated to be present, the gastric juice ontaining free acid corresponding to about 3 per cent. HCl. n the salivary glands of *Dolium galea*, also, 0·4 per cent. HCl is ound along with free sulphuric acid.

Hydrochloric acid is formed synthetically from its elements f they are mixed in equal volumes and exposed to the aylight; upon this action Bunsen and Roscoe's method for easuring the chemical action of light-rays is founded. In the direct light of the sun the two gases unite with an explosion; also by heating and by the action of the electric spark (in the latter case even when much diluted by air), but not by the action platinum sponge.

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[1] Details in Kopp's *Geschichte der Chemie*, iii., p. 346.

The action of light on mixtures of chlorine and hydrogen has been more closely investigated by Gautier and Helier.[1] They found no reaction to take place when the gases were kept in the dark for any length of time; nor was any HCl formed when the gaseous mixture was exposed to the faint light of a candle. Therefore observations can be made with the mixture in such faint light without any danger of an explosion.

A. Coehn and K. Stuckardt[2] have investigated the action of light on the gaseous systems hydrogen iodide, hydrogen bromide, hydrogen chloride, and their components. The reactions were effected by means of a mercury lamp in both quartz and uviol glass apparatus. In all three cases equilibrium was reached from both sides. In quartz apparatus the decomposition proceeds to the extent of 92·3 per cent. in the case of hydrogen iodide, and this is reached in ten minutes; the formation proceeds to 7·6 per cent In both uviol glass and ordinary glass there is a decomposition of 100 per cent. and no formation in the case of hydrogen iodide. With hydrogen bromide there is 100 per cent. decomposition in quartz, 20 per cent. in uviol glass, and no decomposition in glass. The amount of formation of hydrogen bromide is zero in quartz, 80 per cent. in uviol glass, and 100 per cent. in glass. In the case of hydrogen chloride there is 0·42 per cent. decomposition and 99·58 per cent. formation in quartz and 100 per cent. formation with no decomposition in uviol glass and ordinary glass. In the case of hydrogen bromide the reaction is complete in four hours and with hydrogen chloride in less than five minutes. The use of the three types of apparatus shows the effect of the different spectral regions; in quartz, light down to 220 $\mu\mu$ is active, in uviol glass to 254 $\mu\mu$, and in Jena glass down to 300 $\mu\mu$.

Hydrochloric acid is also formed by the action of chlorine on all compounds of hydrogen (except hydrofluoric acid), and especially on organic substances under various conditions;

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[1] *Comptes rend.*, cxxiv., p. 1128.

[2] *Z. physik. Chem.*, 1916, 91, 722-744; *J. Chem. Soc.*, 1917, **112**, ii., 5-6.

also by the action of hydrogen, and especially of hydrogen compounds on many chlorides.

Experiments on the formation of HCl from hydrogen, oxygen, and chlorine under varying conditions are described by Hautefeuille and Margueritte[1]

Density.—The density at 0° is 0·908, at 15° = 0·835.[2] The weight of a normal litre of hydrogen chloride has been determined with great exactness. Q. Scheuer[3] gives as mean value 1·6394 g. per litre. F. P. Burt and R. Whytlaw-Gray[4] give 1·63915 ± 0·00004.

Heat of Formation.—The heat of formation of gaseous HCl from its elements is for 36·5 g. HCl = +22 Cals. at 15°, or +26·0 Cals. at 2000°; that of aqueous hydrochloric acid is = 39·3 Cals. per gram molecule.

Melting and Boiling-points.—Anhydrous hydrogen chloride at the ordinary temperature is a colourless gas, containing 2·74 per cent. by weight of H and 97·26 per cent. Cl. By cold and pressure it is condensed into a liquid which does not immediately redden blue litmus-paper. The vapour pressure of the liquid at $t°$ is as follows:—

$t°$	Atmospheres	$t°$	Atmospheres.
4	29·8	33·4	58·85
9·25	33·9	39·4	66·95
13·8	37·75	44·8	75·20
18·1	41·80	48·0	80·80
22·0	45·75	49·4	84·75
26·75	51·00	50·56	85·33

The melting-point of hydrochloric acid is −111·4° and the boiling-point −83·1° (Ladenburg and Krügel); −82 9° (M'Intosh and Steele). The critical temperature $t_c = +51{\cdot}40° \pm 0{\cdot}10°$ and he critical pressure, $p_c = 81{\cdot}55 \pm 0{\cdot}15$ atmos.[5]

Specific Heat.—The specific heat of the gas at constant pressure (22° to 214°) is 0 1852, and at constant volume 0·175, aking water = 1 (Regnault). *Cf.* M. Pier.[6]

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[1] *Comptes rend.*, cix., p. 641; *J. Soc. Chem. Ind.*, 1890, p. 184.

[2] Ansdell, *Chem. News*, 60, 75.

[3] *Comptes rend.*, 1909, 149, 599.

[4] *Trans. Faraday Soc.*, 1911, 7, 30.

[5] E. Cardoso and A. F. O. Germann, *J. Chim. Phys.*, 1912, 10, 517.

[6] *Z. physik. Chem.*, 1909, 68, 759.

Refractive Index.—The refractive index for the D line at N.T.P. is 1·000447.

Decompositions.—Hydrochloric acid is decomposed by electrolysis, the dry gas only to a small extent. It is also decomposed by long-continued electric or induction sparks, and partially also by heating to 1500° C. Bodenstein and Geiger[1] found that at ordinary temperatures the dissociation is only $6 \cdot 6 \times 10^{-15}$ per cent., at 1000° = 0·002 per cent., and at 2000° = 0·8 per cent. Aqueous hydrochloric acid, exposed to sunlight in a closed bottle for a length of time, gives off free chlorine, which can be detected by gold leaf after a few hours.

Hydrochloric Acid Solution.

Hydrochloric acid has great affinity for water, and condenses with the aqueous vapour of atmospheric air into thick fumes; water absorbs it with considerable evolution of heat; and even borax, magnesium sulphate, or sodium sulphate, containing water of crystallisation, absorb it from gaseous mixtures.

Aqueous hydrochloric acid is colourless, unless it contains impurities; a yellow colour may be caused by ferric chloride, free chlorine, or organic substances. At the freezing-point of mercury it solidifies to a butter-like mass. A concentrated solution fumes in the air. According to H. Deicke, 1 c.c. of water at *t*° and 760 mm. pressure absorbs a number of cubic centimetres of HCl gas, at the same temperature and pressure, shown in the following table at *a*; the resulting aqueous acid has the specific gravity shown at *s*, and contains *c* per cent. of HCl.

t°	a vols.	s.	c per cent. HCl.
0	525·2	1·2257	45·148
4	494·7	1·2265	44·361
8	480·3	1·2185	43·828
12	471·3	1·2148	43·277
14	462·4	1·2074	42·829
18	451·2	1·2064	42·344
18·25	450·7	1·2056	42·283
23	435·0	1·2014	41·536

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[1] *Z. physik. Chem.*, 1904, 49, 70.

Effect of Pressure on Solubility.—The solubility of HCl at a fixed temperature depends on the gaseous pressure. According to Roscoe and Dittmar,[1] 1 gram of water at 0° absorbs G grammes HCl at a total pressure P, as shown by this table:—

P.	G.	P.	G.
mm.	grms.	mm.	grms.
60	0·613	600	0·800
100	0·657	700	0·817
150	0·686	800	0·831
200	0·707	900	0·844
250	0·724	1000	0·856
300	0·738	1100	0·869
400	0·763	1200	0·882
500	0·782	1300	0·895

Effect of Temperature on Solubility.—For a total pressure of 760 mm. the same authors give a table showing the change in the solubility of HCl in water with varying *temperature.*

1 g. of water absorbs at 760 mm. pressure:—

	Grm. HCl.		Grm. HCl.
At 0° C.	0·825	At 32° C.	0·665
„ 4° „	0·804	„ 36° „	0.649
„ 8° „	0·783	„ 40° „	0·633
„ 12° „	0·762	„ 44° „	0·618
„ 16° „	0·742	„ 48° „	0·603
„ 20° „	0·721	„ 52° „	0·589
„ 24° „	0·700	„ 56° „	0·575
„ 28° „	0·682	„ 60° „	0·561

Concentrated aqueous hydrochloric acid on heating l both gas and water, and becomes weaker on boiling, till, according to Bineau, its specific gravity has attained 1·101 and its composition is 20·17 per cent. HCl + 79·82 per cent. H_2O, which exactly corresponds to the formula HCl, $8H_2O$; it then boils at 110° C., and distils without any change. On the other hand, more dilute acid on boiling loses more water than gas, till it reaches exactly the same concentration. Roscoe and Dittmar found that for every fixed pressure there is a constant-boiling mixture. The constant-boiling mixture at 760 mm. contains 20·24 per cent. HCl, but at a lower pressure the acid distilling unchanged is stronger, whilst at a higher pressure it is weaker, as shown by the following table:—

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[1] *Ann. Chem. Pharm.*, cxii., p. 327.

Gaseous pressure.	HCl.	Gaseous pressure	HCl.	Gaseous pressure.	HCl.
Metres.	Per cent.	Metres.	Per cent.	Metres.	Per cent.
0·05	23·2	0·8	20·2	1·7	18·8
0·1	22·9	0·9	19·9	1·8	18·7
0·2	22·3	1·0	19·7	1·9	18·6
0·3	21·8	1·1	19·5	2·0	18·5
0·4	21·4	1·2	19·4	2·1	18·4
0·5	21·1	1·3	19·3	2·2	18·3
0·6	20·7	1·4	19·1	2·3	18·2
0·7	20·4	1 5	19·0	2·4	18·1
0·76	20·24	1·6	18·9	2·5	18·0

According to Bineau, when strong acid is exposed to the air, it gradually loses HCl till it reaches the sp. gr. 1·128 at 15° C.; it then contains 25·2 per cent. HCl, corresponding to the formula $HCl, 6H_2O$, and boils at 106°C. with a loss of gas. Here also the temperature plays an important part. On passing a stream of air through hydrochloric acid, part of the latter is evaporated; for each temperature an acid of a definite composition remains behind, which then evaporates unchanged; stronger or weaker acid changes its composition, until that point has been reached which corresponds to the temperature in question, as indicated by the following table (by Roscoe and Dittmar):—

Temp., degrees.	HCl, per cent.	Temp., degrees.	HCl, per cent.	Temp., degrees	HCl, per cent.
0	25·0	35	23·9	70	22·6
5	24·9	40	23·8	75	22·3
10	24·7	45	23·6	80	22·0
15	24·6	50	23·4	85	21·7
20	24·4	55	23·2	90	21·4
25	24·3	60	23·0	95	21·1
30	24·1	65	22·8	100	20·7

Hence the acid distilling at a certain pressure without change, that is, at a constant temperature, is identical with the acid which remains unchanged when a current of dry air is passed through hydrochloric acid at the same temperature and at ordinary pressure. This is shown by the following table:—

Pressure, metres.	Boiling-point, degrees.	HCl, per cent.	Temperature of the air-current, degrees.	HCl, per cent.
0·10	61 to 62	22·8	62	22·9
0·21	76 „ 77	22·1	77	22·2
0·30	84 „ 85	21·7	85	21·7
0·38	91	21·3	91	21·4
0·49	97	20·9	98	21·1
0·62	103	20·6	...	...

Further investigations on the conditions of the equilibrium between the solid, liquid, and gaseous states of hydrochloric acid have been made by Roozeboom[1] and by R. B. Warder[2]

A solid *dihydrate*, $HCl, 2H_2O$, with 50·35 per cent. HCl, crystallises at −17·7°. Pickering[3] found also a *trihydrate*, with 40·33 per cent. HCl, crystallising at −24·4°. F. F. Rupert[4] has shown that a monohydrate also exists. It has a density of 1·48 and freezing-point of −15·35° with a vapour pressure of approximately 17·3 atmos. With greater dilution the freezing-point sinks lower and lower; acid containing 30·3 per cent. does not crystallise even at −83°. With only 23·9 per cent. HCl crystallisation sets in at −79°, but this mostly consists of water; from this point the freezing-point gradually rises again.

Specific Gravities of Hydrochloric Acid.—Tables of densities are given by Davy, Kirwan, Dalton, and Ure; the last of these was frequently used in England, although it had been rendered obsolete by that of J. Kolb,[5] reprinted in prior editions of this work. This table has now been replaced by that worked out by Lunge in conjunction with Marchlewski.[6] In making use of this (p. 44), we must, of course, recollect that it refers to *chemically pure* hydrochloric acid, and that commercial acids will always contain less HCl than indicated by the table for any given specific gravity. "Roaster-acid" often contains several per cent. sulphuric acid besides solid matter. The table in question refers to a temperature of

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[1] *Z. physik. Chem.*, 1887, p. 365, and 1888, p. 459.

[2] *Chem. News*, 1891, lxiii., p. 17.

[3] *Ber.*, 1893, p. 279.

[4] *J. Amer. Chem. Soc.*, 1909, 81, 851.

[5] *Comptes rend.*, 74, 337.

[6] *Z. angew. Chem.*, 1891, p. 133.

15°; the changes of the specific gravity brought about by higher or lower temperatures are indicated in Table II. on p. 45.

I. *Specific Gravity of Hydrochloric Acid at* 15° C. *compared with Water at* 4° *and reduced to Vacuum.*

(Lunge and Marchlewski.)

Degrees Twaddell.	Specific gravity at $\frac{15^\circ}{4^\circ}$ *in vacuo.*	100 parts by weight correspond to parts by weight of			1 litre contains grms. HCl.	1 cubic foot contains lb. of HCl.
		HCl.	Acid of spec. grav. 1·1425 = 28·5° Twaddell.	Acid of spec. grav. 1·152 = 30·4° Twaddell.		
0	1·000	0·16	0·57	0·53	1·6	0·10
1	1·005	1·15	4·08	3·84	12	0·75
2	1·010	2·14	7·60	7·14	22	1·37
3	1·015	3·12	11·80	10·41	32	1·99
4	1·020	4·13	14·67	13·79	42	2·62
5	1·025	5·15	18·30	17·19	53	3·30
6	1·030	6·15	21·85	20·53	64	3·99
7	1·035	7·15	25·40	23·87	74	4·61
8	1·040	8·16	28·99	27·24	85	5·30
9	1·045	9·16	32·55	30·58	96	5·98
10	1·050	10·17	36·14	33·95	107	6·67
11	1·055	11·18	39·73	37·33	118	7·35
12	1·060	12·19	43·32	40·70	129	8·04
13	1.065	13·19	46·87	44·04	141	8·79
14	1·070	14·17	50·35	47·31	152	9·48
15	1 075	15·16	53·87	50·62	163	10·16
16	1·080	16·15	57·39	53·92	174	10·85
17	1·085	17·13	60·87	57·19	186	11·59
18	1·090	18·11	64·35	60·47	197	12·28
19	1·095	19·06	67·73	63·64	209	13·03
20	1·100	20·01	71·11	66·81	220	13·71
21	1·105	20·97	74·52	70·01	232	14·46
22	1·110	21·92	77·89	73·19	243	15·15
23	1·115	22·86	81·23	76·32	255	15·90
24	1·120	23·82	84·64	79·53	267	16·65
25	1·125	24·78	88·06	82·74	278	17·33
26	1·130	25·75	91·50	85·97	291	18·14
27	1·135	26·70	94·88	89·15	303	18·89
28	1·140	27·66	98·29	92·35	315	19·64
29	1·145	28·61	101·67	95·52	328	20·45
30	1·150	29·57	105·08	98·73	340	21·20
31	1·155	30·55	108·58	102·00	353	22·01
32	1·160	31·52	112·01	105·24	366	22·82
33	1·165	32·49	115·46	108·48	379	23·63
34	1·170	33·46	118·91	111·71	392	24·44
35	1·175	34·42	122·32	114·92	404	25·19
36	1·180	35·39	125·76	118.16	418	26·06
37	1·185	36·31	129·03	121·23	430	26·81
38	1·190	37·23	132·30	124·30	443	27·62
39	1·195	38.16	135·61	127·41	456	28·43
40	1·200	39·11	138·98	130·58	469	29·24

II. *Influence of Temperature on the Specific Gravity of Hydrochloric Acid.*

The column *a* shows the specific gravities at $\frac{15^\circ}{4^\circ}$; the columns Δ show the amounts to be added or subtracted to correct the specific gravity to the temperature indicated.

a	Δ 0°	Δ 10°	Δ 20°	Δ 30°	Δ 40°	Δ 60°	Δ 70°
1·160	+ 0·008	+ 0·003	− 0·003	− 0·008	− 0·013	− 0·018	− 0·022
1·150	0·008	0·003	0·003	0·008	0·013	0·018	0·022
1·140	0·008	0·003	0·003	0·008	0·013	0·017	0·022
1·130	0·008	0·003	0·003	0·008	0·013	0·018	0·021
1·120	0·008	0·003	0·003	0·008	0·012	0·017	0·020
1·110	0·008	0·003	0·003	0·008	0·011	0·016	0·021
1·100	0·008	0·003	0·003	0·008	0·012	0·016	0·021
1·090	0·008	0·003	0·003	0·008	0·013	0·017	0·020
1·080	0·008	0·003	0·003	0·008	0·012	0·016	0·021
1·070	0·008	0·003	0·003	0·007	0·011	0·015	0·020
1·060	0·008	0·003	0·003	0·007	0·012	0·016	0·021
1·050	0·008	0·003	0·003	0·007	0·012	0·017	0·022
1·040	0·008	0·003	0·003	0·007	0·013	0·018	0·022
1·030	0·008	0·003	0·003	0·008	0·013	0·018	0·022
1·020	0·008	0·003	0·003	0·008	0·013	0·018	0·022
1·010	0·008	0·003	0·003	0·008	0·013	0·018	0·022

Another table for the same purpose, the arrangement of which may be preferred by some readers, is given in Lunge's *Technical Chemists' Handbook*, 1916, p. 153.

The *specific heats* of hydrochloric acid of various concentrations are given as follows by Hammerl[1]:—

HCl, per cent.	Specific heat.	HCl, per cent.	Specific heat.
32·37	0·6260	18·30	0·7502
28·18	0·6602	12·50	0·8132
25·37	0·6797	6·53	0·8983
23·82	0·6895	4·8	0·9310

Electrolysis of Hydrochloric Acid Solution.—Hydrochloric acid is an excellent conductor and on electrolysis of concentrated solutions yields hydrogen and chlorine. According to E. Doumer[2], when a solution of hydrogen chloride is electrolysed, the theoretical weight of hydrogen is evolved at the negative

[1] *Comptes rend.*, lxxxix., p. 902.

[2] *Comptes rend.*, 1908, 146, 329.

electrode and a mixture of chlorine and oxygen at the positive electrode. The proportion of oxygen increases in weaker solutions of acid, reaching as much as one-quarter of the whole. This liberation of oxygen cannot be attributed to the secondary action of the chlorine formed on the solvent water; on the contrary the chlorine combines with a certain amount of the oxygen forming oxides. When silver or mercury anodes are employed, which fix the chlorine, a larger volume of oxygen is obtained than with platinum anodes. Not only the hydrochloric acid but also the water is decomposed electrolytically. For a criticism of some points in Doumer's paper, see T. Guilloz.[1]

F. H. Jeffery[2] electrolysed hydrochloric acid solution with a copper anode in an atmosphere of nitrogen. He found that the copper went into solution as complex anions, corresponding, in presence of excess of hydrochloric acid, to the compound H_2CuCl_3. Black metallic copper was deposited from disintegration of the anode, and a precipitate of cuprous chloride was formed, no chlorine being evolved during the electrolysis.

The migration ratio of dilute solutions of hydrochloric acid has been determined by C. Chittock[3] who found that the transport ratio of the Cl ion increases from 0·171 at a concentration of 0·001405 equivalents per litre to 0·275 at a concentration of 0·0001006.

Chemical Reactions of Hydrochloric Acid.

Hydrochloric is a very strong acid, which even in a very highly diluted state still reddens blue litmus-paper, and has a strongly acid taste. It dissolves most metallic oxides, forming chlorides, also many metals with evolution of hydrogen, especially all metals soluble in dilute sulphuric acid. Lead also, which is scarcely at all attacked by dilute sulphuric acid, is quickly corroded and dissolved by somewhat concentrated and hot hydrochloric acid; accordingly, lead vessels, pipes, etc., are to be avoided as much as possible in its condensation or employment.

Of great importance is the action exerted by hydrochloric acid upon compounds very rich in oxygen, viz., upon the peroxides of manganese and lead, chromic acid and its salts, nitric acid, etc. In all these cases, but in some only on heating, part of the hydrochloric acid is oxidised to free chlorine and water. Upon this reaction is founded the industrial preparation of chlorine, as well as the solvent action of aqua regia (*i.e.*, of a mixture of nitric and hydrochloric acids) upon gold, platinum, etc. Hydrochloric acid also expels most other acids from their salts. Many natural silicates, especially the zeolites, and also artificially prepared ones (slags), are decomposed by digestion with HCl with formation of gelatinous silica, the soluble silicates of potassium and sodium being of course the most easily decomposed. Phosphoric, boric, carbonic, etc., acids are frequently liberated by hydrochloric acid. Thomsen has shown, by thermochemical experiments, that in dilute solutions hydrochloric acid possesses twice the affinity of sulphuric acid, *i.e.*, in a mixture of one equivalent of hydrochloric acid, one equivalent of sulphuric and one equivalent of a base, the hydrochloric acid neutralises two-thirds of the base and the sulphuric acid one-third. Although hydrochloric acid is a considerably stronger acid than sulphuric acid, most chlorides are decomposed readily on gentle warming with concentrated sulphuric acid, yielding sulphates and hydrochloric acid. This is to be expected from the Law of Mass Action, as under the conditions of the experiment the volatile hydrochloric acid escapes constantly from the mixture and consequently the reaction proceeds in this direction. The reaction can in many cases (possibly in all) be reversed by keeping up a sufficient partial pressure of HCl.

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[1] *Comptes rend.*, 1908, 146, 581.

[2] *Proc. Faraday Soc.*, Oct. 1915.

[3] *Proc. Camb. Phil. Soc.*, 1909, 15, 55.

Boussingault[1] has made direct experiments on the decomposition of sulphates by HCl at a higher temperature. But most conclusive are the results obtained by Hensgen[2] from the action of dry gaseous HCl upon different sulphates. Potassium sulphate is not sensibly decomposed either in the cold or at 100°; but a little below a dark red heat, almost a quantitative decomposition into chloride and free sulphuric acid, sets in. Anhydrous sodium sulphate behaves in the same way; but crystallised sodium sulphate (Na_2SO_4, 10 H_2O) is completely converted into NaCl by a current of hydrochloric acid gas at ordinary temperatures, and even at $-17°$ C. It first melts in its water of crystallisation; and afterwards the temperature rises to 53° or 55° C. Lithium sulphate was also decomposed completely, the sulphates of barium, strontium, and calcium nearly but not quite completely. Cupric sulphate, either anhydrous or containing only one molecule of H_2O, with dry HCl, seems to form an addition-product of the formula $CuSO_4$, $2HCl$, which in dry air over quicklime parts with all its acid again, but when heated in a current of air or oxygen gives off free chlorine and water; this probably plays an important part in Deacon's chlorine process.

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[1] *Comptes rend.*, lxxviii., p. 593.

[2] *Ber.*, ix., p. 1671.

It should be remarked that in these experiments the sulphates were exposed to a large excess of hydrochloric acid in an atmosphere of this gas. The reaction therefore proceeds differently to its course under normal conditions. When a chloride, say NaCl, is brought into contact with sulphuric acid, he HCl is, at least partly, liberated, and on raising the emperature can be *completely* expelled, because after the free HCl is expelled the H_2SO_4 can decompose a fresh portion of he chloride.

With sulphur trioxide, hydrochloric acid gas yields chlorosulphuric acid, a strongly fuming liquid.

Hydrochloric acid shows *antiseptic* properties in quantities of ess than 0·5 per cent.[1] It acts as a strong poison on plants, and s therefore a very noxious part of the chimney gases escaping from chemical works. (*Cf.* p. 226.)

The action of hydrochloric acid on the animal organism has been studied by Lehmann.[2] Even with only 0·01 per cent. HCl in the air, irritation was produced; with 0·1 to 0·15 per cent., animals died in a few hours. A strong man found air with 0·004 per cent. HCl unbearable. In no case should factory air ever contain more than 0·01 per cent. HCl.

Non-aqueous Solutions.—Hydrochloric acid is readily soluble n most alcohols; in benzene and its homologues; and also n ether, acetone, and many other solvents. The solution of hydrochloric acid in absolutely anhydrous solutions is usually much less active chemically than the aqueous solution, and it has even been stated that an anhydrous ethereal solution will not act on metallic sodium. The presence of a trace of water causes the non-aqueous solutions to react much like the aqueous solutions.

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[1] Sieber, Liebig's *Jahresber.*, 1879, p. 1020.

[2] *Arch. Hygiene*, 1886, p. 16.

Hydrochloric acid is readily absorbed by charcoal, the amount depending on the nature of the charcoal; wood-charcoal was found to absorb about 160 times its own volume of the gas.

CHAPTER II

THE RAW MATERIALS AND PRODUCTS OF THE MANUFACTURE OF SALTCAKE AND HYDROCHLORIC ACID AND THEIR ANALYSIS

ONLY a small quantity of sodium sulphate is prepared in the crystallised state as Glauber's salt, principally that intended for freezing-mixtures and pharmaceutical purposes; the rest is made as calcined sulphate or "saltcake," one portion of it being used as such (for instance, in glass-making), another portion being at once converted into alkali. The proportions have changed very much in the course of time, and very little is now converted into alkali.

The different processes for preparing sulphate of soda may be divided into those in which it is the principal product, and those in which it is a by-product. As the principal product, nearly all the saltcake is obtained by decomposing common salt with sulphuric acid, or common salt with sulphurous acid in the presence of air (according to Longmaid, Hargreaves, etc.). We shall treat of the latter processes later on; at present we will turn our attention to the ordinary process of decomposing common salt by sulphuric acid.

This is not merely the process which up to this day furnishes the largest portion of all sodium sulphate, but at the same time is the oldest, viz., that employed by Glauber himself. He and his successors obtained sodium sulphate in the first instance as a by-product in making hydrochloric acid in glass retorts. But when the manufacture of artificial soda, at the end of the eighteenth century, received a sudden impetus, that of sulphate had to be increased in the same proportion; and the time came when muriatic acid became a by-product, and in many cases was altogether lost—a state of things which probably does not exist anywhere at the present day. Leblanc himself prepared the sulphate which served as a starting-point for his soda-process by decomposing common salt with sulphuric acid.

As the scale of manufacture increased the form of the apparatus was changed. At first iron cylinders were used where the muriatic acid had to be condensed, or open lead dishes where this was not the case; the latter were frequently heated by the waste fire of the soda-furnaces, and were usually combined with a calcining-furnace. But only when alkali-manufacture had gained a firm footing in England, and began to be carried on there on a much larger scale than on the Continent, was apparatus adopted suitable for producing large quantities. The first in England to make saltcake by decomposing common salt with sulphuric acid was William Losh, who had studied chemistry in France, and, having returned to his native country in the beginning of this century, erected a chemical works at Walker-on-Tyne. A weak-brine spring existing there first gave occasion to this. In 1812 or 1815 lead chambers were erected, the product of which was partly sold as oil of vitriol, partly employed for decomposing common salt obtained from various sources. The first furnaces for this purpose were made of lead and lined with bricks; 2 cwt. of salt were introduced at a time, and the vitriol was slowly poured in from a carboy through a hole in the furnace-roof. The muriatic acid escaped into the air by a short chimney. After three hours a plug in the side of the lead pan was drawn out and the semi-liquid mass was run into a lead vessel, where it solidified into a hard cake, which was broken up and calcined to finished saltcake. The lead furnace, which stood a very short time, was in 1828 replaced by a brick furnace, and in 1840 by cast-iron decomposing pans.[1] A second factory of a similar kind arose at Blyth in 1822, but 1823 was the real year of birth of the manufacture of saltcake and carbonate of soda on a large scale. In that year the enormous salt-duty, which had prevented any great extension, was taken off, and James Muspratt erected a factory at Liverpool, in which common salt was decomposed with sulphuric acid, and Leblanc's process was carried out completely.

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[1] Clapham, *Soda Manufacture on the Tyne*, p. 14.

In the same year Cookson & Co. (now the Jarrow Chemical Company), started operations at South Shields; and in 1827 a number of works were erected both in Lancashire and on the Tyne.

Except in very few cases, viz., the cylinder furnaces of the oldest and the mechanical furnaces of the most recent time, *the operation of making saltcake* consists of *two stages.* The common salt is at once brought together with the whole quantity of sulphuric acid required—that is, $1H_2SO_4$ to $2NaCl$, which ought to yield simply Na_2SO_4 and $2HCl$; but, owing to the tendency of sulphuric acid to form acid salts, the decomposition proceeds in stages. The usual representation of the process is that at first the following reaction takes place:—

$$\text{I.}\quad \underset{\substack{\text{Common}\\ \text{salt.}}}{NaCl} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Acid sodium}\\ \text{sulphate.}}}{NaHSO_4} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{HCl}$$

and that then a second molecule of common salt comes into play, and the following reaction sets in—

$$\text{II.}\quad \underset{\substack{\text{Acid sodium}\\ \text{sulphate.}}}{NaHSO_4} + \underset{\substack{\text{Common}\\ \text{salt}}}{NaCl} = \underset{\substack{\text{Sodium}\\ \text{sulphate.}}}{Na_2SO_4} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{HCl.}$$

These two reactions, however, are not sharply separated. On the whole, however, at a comparatively low temperature sulphuric acid and common salt, even when the latter is in excess, act upon each other *principally* according to the first equation, whilst at a higher temperature the excess of common salt acts upon the acid sodium sulphate according to the second equation. In other words, the decomposition of common salt becomes *complete* only at a higher temperature, viz., at a pretty strong red heat The results obtained in practice do not agree with the above equations. According to the first equation, only 50 per cent. of all the hydrochloric acid ought to be given off in the *technical* first stage, which is going on in the decomposing-pan, but it is found that 66 to 70 per cent. of the HCl is given off, although nothing like a red heat is attained there.

According to Volney,[1] the first stage in the action of concentrated sulphuric acid on sodium chloride at 18° C. is represented by this equation :—

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[1] *J. Amer. Chem. Soc.*, **23**, 820.

$$2NaCl + 2H_2SO_4 = NaH_3(SO_4)_2 + HCl + NaCl.$$

When this is over, no more gas is given off in the cold. Only on heating does the second stage set in as follows :—

$$NaH_3(SO_4)_2 + NaCl = 2NaHSO_4 + HCl,$$

and the temperature now rises to about 120° C.

Thus by the action of liquid sulphuric acid on solid common salt there is always formed, first, sodium sulphate (whether acid or neutral), which is solid, and secondly, hydrogen chloride, which escapes as a gas and has to be condensed into a liquid, along with aqueous vapour coming from the water always present in sulphuric acid. The strongest sulphuric acid is never employed, but acid of at most 144° Tw. = 78 or 80 per cent. H_2SO_4 and 22 to 20 per cent. of H_2O. The common salt also contains more or less water. The *water* is mostly not given off in the first stage of the operation (that is, in the pan) but in the second (the calcining-furnace or roaster); when employing dilute sulphuric acid, however, a good deal of water must be driven off even in the pan. As steam on being condensed to liquid water gives out a good deal of heat, and as cooling is one of the principal conditions of effective condensation of muriatic acid, this condensation is much more difficult when dilute sulphuric acid has been employed for decomposing the salt.

The important part played by the *air* mixed with the HCl and the steam will be explained later.

At present we need only remember that, along with the preparation of sodium sulphate, the *condensation of hydrochloric acid* must always be effected, to prevent the escape of this noxious gas, whether or not the condensed muriatic acid can be sold, or used by the manufacturer himself.

If *hydrochloric acid is the principal product*, a different style of working is adopted. Instead of employing more than $1H_2SO_4$ to $2NaCl$, as is sometimes recommended, *less* sulphuric acid is used than is required by theory. In the former case all the hydrochloric acid would be completely expelled, but it would be contaminated by sulphuric acid escaping at the same time. With excess of salt a little common salt remains undecomposed, but the hydrochloric acid will be quite free from sulphuric acid, and as sulphuric acid is nearly everywhere the dearer of the two ingredients, an excess of common salt will be employed if the value of the hydrochloric acid is the principal thing and that of the residue of (impure) sodium sulphate only a secondary consideration. This is the case in all places where, owing to the high price of coal, the consumption of sodium sulphate for making glass or alkali is excluded, or where hydrochloric acid is required for other purposes, whilst its transit from the centres of chemical industry is extremely dear, making its local production as a principal matter remunerative.

The raw materials for the manufacture of sulphate of soda are the following:—first, *sodium chloride* with more or less of impurities, as common salt or rock-salt; secondly, *sulphuric acid;* thirdly, in many cases, *cylinder-cake, nitre-cake*, and other products containing sodium sulphate, free salt or free acid (residues from the manufacture of muriatic acid in cylinders and from that of nitric acid, the pan-scale of salt-works, etc.). (The "saltpetre-salt" obtained in making nitrate of potash from potassium chloride and nitrate of soda is, owing to a percentage of 0·5 of saltpetre, unfit for making saltcake; it acts strongly upon the pans, tools, etc, and the hydrochloric acid contains chlorine.) The materials mentioned in the third place always play a secondary part, and are nearly always used as an addition to common salt, with a corresponding change in the amount of sulphuric acid. Thus common salt and sulphuric acid remain the principal raw materials for the saltcake manufacture.

I. *Salt* (*sodium chloride*) has been described in detail, p. 4 *et seq.* Here we have only to consider which of the various technical forms of sodium chloride are most suitable for the saltcake manufacture. *Brine* is not employed for this purpose at all.

Rock-salt is decidedly an inferior material for the manufacture of saltcake, if it contains any quantity of impurities. Thus the great bulk of the Stassfurt salt is contaminated by calcium sulphate; a great deal of the Cheshire rock-salt contains too much ferric oxide, and so forth. But other descriptions of rock-salt leave nothing to be desired in the matter of purity, as, for instance, the salt of Neu-Stassfurt. Such rock-salt has the great advantage of being almost free from moisture, and consequently very strong (98 to 99 per cent.) and of quite regular composition, thus greatly facilitating the process. But all rock-salt labours under the disadvantage that it must be ground before putting it into the decomposing-pans, and that this must not be done too finely, since otherwise the salt lies as a dead mass at the bottom of the pan and is not penetrated by the acid. To avoid this, the salt is crushed only roughly, and the fine powder (below ⅛-inch) is separated by a sieve with ⅛-inch meshes. It was formerly held, but is not confirmed by German experts, that rock-salt is more difficult to decompose than pan-salt. The former requires more frequent and careful stirring than the latter, a matter of less importance if mechanical decomposing-pans are used. In the Hargreaves process (Chapter V.) rock-salt and pan-salt are frequently mixed. Where salt has to be used in solution, as is the case in the ammonia-soda process, rock-salt will do perfectly well, and even the anhydrous calcium sulphate is then left behind. The red rock-salt of Cheshire is hardly usable at all for decomposing, and clay or magnesium chloride in rock-salt may also prevent its use.

Sea-salt is generally made in different grades. That which crystallises first contains a little gypsum, but is otherwise pure, and is generally set apart for consumption with food. The second quality, that which crystallises between sp. gr. 1·23 and 1·25, contains very little $CaSO_4$, but about 1 per cent. $MgCl_2$, and is rather damp. It is much improved by allowing it to lie in great heaps in the open air through the winter months; the rain then washes out most of the impurities, together with several per cent. of NaCl, and converts the small crystals into larger lumps, of the size of a pea to that of a walnut, which are, however, of much looser texture than rock-salt, and readily dissolve in the decomposing-pan. This salt is excellent for making ammonia soda as well.[1]

Pan-salt, on account of its physical structure, is of all salts that best adapted for decomposing. The loose crystals formed during the evaporation of the brine form a kind of sponge, which in the decomposing-pan absorbs the acid and quickly dissolves in it, thus greatly facilitating the work. It has the drawback of frequently containing impurities, as well as very varying quantities of water.

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[1] *Cf.* Lunge, *Chem. Industrie*, 1883, p. 228.

The porous nature of pan-salt is recognised by the fact that a cubic foot of it on the average weighs 43 lb., whilst coarsely crushed rock-salt weighs from 76 to 84 lb., and finely ground rock-salt 70 lb. This is to be considered in calculating railway freights, in stock-taking, and so forth.

By "pan-salt" we here understand merely the coarse-grained common salt which is obtained by evaporating the brine below its boiling-point. That kind of salt which is obtained in boiling, and which is of a very fine grain ("butter-salt"), is not suitable for use in the decomposing-pan, but can be employed in the Hargreaves process.

II. The *sulphuric acid* used for decomposing salt is always the common chamber-acid, or the acid obtained by evaporation in lead pans or in the Glover tower. The usual impurities do no harm in the manufacture of saltcake; except for that which is destined for glass-making, when acid containing iron should be avoided. The arsenic contained in the sulphuric acid does not remain in the saltcake, but passes over into the muriatic acid, and its presence in this may sometimes be inconvenient. Nitrogen and lead compounds in ordinary vitriol occur in too small quantities to do any harm.

Of greater importance is the *concentration* of the sulphuric acid employed. The best strength is from 140° to 144° Tw. Stronger acid, even if it can be obtained without any further expense (for instance, by a Glover tower), is not good for the process, because the hydrochloric acid is given off too vehemently and the mass solidifies too quickly, before it has been thoroughly mixed and decomposed. The drawback of too great concentration is certainly easily remedied by adding chamber-acid, and this is regularly done at the factories working with a Glover tower. But the opposite drawback of too much dilution is not so easily avoided in the absence of a Glover tower, and if it is too expensive to concentrate the acid in lead pans. No expenditure should be needed for this, however, as the chamber-acid can be concentrated to 144° Tw. on the top of the pyrites-burners. But before this was well known, to avoid the expense of concentration by additional fuel, the chamber-acid was taken directly for the decomposing process at many works. So long as its strength is not below 128°, or, *at least*, 124° Tw., no great harm is done, but the work is slower and the condensed muriatic acid rather weaker. Those manufacturers who do not get the chamber acid up to at least 124° Tw. ought not to shirk the expense of concentration, even if they possess no pans on the burners and no Glover tower; for weaker acid not only retards the operation very much, makes the condensation more difficult, and yields weaker muriatic acid, but it also causes greater wear and tear of the decomposing-pans. This case may occur in starting factories before the plant is in proper working order; sometimes, for days or even for weeks they must work with acid of, say, 106° Tw.; but such a proceeding is generally paid for by a quick destruction of the decomposing-pans. The sulphuric acid may be moderately preheated by the waste fire gases from the saltcake furnaces.

Analysis of the Raw Materials and Products.

This section is confined to the substances described in the preceding pages; the analytical methods for the intermediate products formed in the course of manufacture, of the liquors, etc., will be described subsequently. Fuller details than are given here will be found in G. Lunge, *Technical Chemists' Handbook*, London, Gurney & Jackson, 1908; G. Lunge, *Technical Methods of Chemical Analysis*, English translation, edited by C. A. Keane, vol. i., Gurney & Jackson, 1908.

The descriptions of the methods of analysis are written on the assumption that the analyst has already had a training equivalent to that covered by Cumming and Kay's *Quantitative Analysis*, Oliver & Boyd, 1919.

Analysis of Common Salt.

A complete analysis of common salt is but rarely performed in alkali-works. Where the salt is always bought from the same source, the buyer is usually content with simply estimating the moisture; and in the case of pure dry rock-salt even this may be dispensed with. Impure rock-salt must be examined for its accessory substances, of which calcium sulphate is the most important. Apart from this, it is useful to examine for magnesia. Any excess of sulphuric acid over that equivalent to the lime and magnesia present is calculated as sodium sulphate. Insoluble substances, as clay and the like, ought never to occur in sensible quantities in salt intended for alkali-works. An examination for potash, iron, etc., is rarely required.

Moisture is estimated by very gradually heating 5 g. in a platinum crucible, taking care to keep the cover on in order to avoid loss by the projection of small particles (*cf.* p. 4); at the end the crucible is brought to a low red heat for a few minutes. It is useful to employ as new a crucible as possible, and to place the stand with the Bunsen burner, etc., on a sheet of black glazed paper, in which case the loss by projection will not exceed 0·1 per cent. Where many samples, especially of damp salt, have to be tested, it is expedient to proceed as follows:—The various samples are weighed in perfectly dry Erlenmeyer flasks, holding 250 c.c., and covered with a small funnel. These flasks are heated on a sand-bath to 140° or 150°. Within three or four hours the water present as "moisture" is evaporated and is estimated by reweighing the flasks after cooling. The "chemically combined" water (from gypsum, etc.) can be estimated by further heating the dry flasks on a wire gauze, but as its quantity is mostly under 0·1, and hardly ever over 0·2 or 0·3 per cent., this operation is usually omitted.

Chloride is estimated by precipitating the filtered solution, after addition of pure nitric acid, with silver nitrate and weighing the silver chloride; or, more expeditiously, although not quite so accurately, by titrating the neutral solution with decinormal silver solution, employing a little yellow potassium chromate as indicator, and going on till the white precipitate turns faintly pink, and retains this tint even after shaking up. The quantity of silver nitrate used is diminished by 0·2 c.c., to allow for the excess causing the coloration, and each cubic centimetre of the remainder is put = 0·003545 g. Cl or 0·00585 g. NaCl. Some people are not able to notice the change of colour quickly enough, and these will always obtain too high results. The change of colour is seen much better if sodium arsenate be used as indicator; in this case a single drop of the silver solution in excess causes a distinct pink coloration, and no deduction must be made for an excess causing the coloration.

Lime is estimated by dissolving the sample completely, adding a little dilute hydrochloric acid, and heating, in case of need, until all calcium sulphate is sure to have been dissolved. The solution is filtered from any clay, etc., the lime is precipitated as oxalate by ammonia and ammonium oxalate, and the precipitate is strongly ignited in order to convert it into CaO, which is weighed and is calculated as such or as $CaSO_4$ (1000 CaO = 2428 $CaSO_4$).

Magnesia is precipitated from the filtrate from the calcium oxalate by the usual phosphate mixture, and is calculated as $MgSO_4$; if, however, the amount of sulphate is less than the equivalent of the CaO and MgO, the remainder of the latter is calculated as $MgCl_2$.

The estimation of *Sulphate* is described in *Sulphuric Acid—Chamber Process.*

J. and S. Wiernik[1] point out that the magnesium chloride in common salt and in brine ought to be directly estimated, as the usual method of calculation just described may involve serious errors. They extract the dry salt with absolute alcohol (sp. gr. 0·796), which dissolves nothing but $MgCl_2$, and continue this operation so long as any chloride is found in the washings. The liquor is freed from alcohol, and the magnesia is estimated as pyrophosphate, and the chlorine by titration. These two ought to agree as regards $MgCl_2$. In the original solution the quantity of magnesia, lime, chlorine, and sulphuric acid is estimated as usual. The SO_3 is first calculated for CaO, then for any MgO present in excess of that found as $MgCl_2$; any excess of SO_3 is calculated as Na_2SO_4. The chlorine corresponding to the $MgCl_2$ present is deducted from the total chlorine, and the remainder is calculated as NaCl.

Ferric oxide and *Alumina* occur very rarely in appreciable quantities. When present, they are found in the hydrochloric-acid solution, filtered from the insoluble residue, and precipitated by adding ammonia free from carbonate—that is, before precipitating the lime as oxalate. Alumina and ferric oxide are best weighed together, and the iron is estimated in a separate sample, by titrating with potassium bichromate after reduction with zinc.

Analysis of Brine.—In this volume we treat solely of methods employing solid salt, but for the sake of completeness, the analysis of brine will be briefly described. First of all the *specific gravity* is taken, observing the temperature. From this, after reducing it to the normal temperature, the percentage of sodium chloride can be ascertained, in the case of very pure brine, by the aid of the table given on p. 8. In the case of impure brine, the composition of which does not, as a rule, vary greatly, if taken from the same source, the specific gravity gives at least an indication of the uniformity of its quality.

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[1] *Z. angew. Chem.*, 1893, p. 43.

If the brine has to be accurately analysed, we estimate chloride, sulphuric acid, lime, and magnesia according to the methods described above, and calculate in the same way. The method of J. and S. Wiernik (*cf. supra*) must be carried out with the residue left on evaporating the brine on a water-bath. Alumina and iron must be estimated, if present.

In brine, calcium, magnesium, and iron may also occur as bicarbonates. These are estimated in a separate sample, by concentrating 500 c.c. in a porcelain capsule to about 100 c.c., filtering the precipitate formed, washing, dissolving it in hydrochloric acid, and estimating therein CaO, MgO, and Fe by the well-known methods. They are calculated as normal carbonates ($CaCO_3$, etc.), and are deducted from the totals otherwise found. For ordinary purposes it is sufficient to dissolve the washed precipitate on the filter in standard hydrochloric acid, and to calculate every cubic centimetre of normal HCl neutralised $=0\cdot0500$ g. $CaCO_3$.

Analysis of Sodium Sulphate.

Pure sodium sulphate is quite white, forms a clear solution in water, has a neutral reaction, shows no trace of chloride when treated with silver nitrate, and yields no precipitates with sulphuretted hydrogen, ammonium sulphide, sodium or ammonium carbonate, or potassium ferrocyanide. Commercial sulphate is tested in the following way:—Usually only the foreign constituents are estimated, and the pure Na_2SO_4 calculated from the difference. If it is merely required to test the *sulphate for one's own use* (for alkali-making), where it is only a check on the manufacture, the following simple process is sufficient:—Twenty grammes of sulphate are weighed, dissolved in 250 c.c. warm water, 50 c.c. taken out with a pipette, and, after methyl-orange[1] has been added, "*free acid*" is titrated using normal caustic-soda solution, of which 1 c.c. corresponds to 1 per cent. SO_3 when working in the above way. In reality the "free acid" includes any HCl, as well as half of the sulphate in $NaHSO_4$, and the salts of alumina and ferric oxide possessing an acid reaction. The influence of the last-mentioned salts on the indicators is irregular, especially in the cold; as they are never present in any considerable quantity, this is not of much consequence, and their effect is entirely avoided by working in the following way. No indicator at all is used, but standard soda solution is added until the first flakes of a permanent precipitate appear, which do not redissolve on agitation. This method is not absolutely exact, but is sufficient for practical purposes.

Sodium chloride is found by taking another 50 c.c. of the above solution, adding exactly as much caustic-soda solution as had been used in the test for free acid, then a few drops of a solution of yellow potassium chromate or of sodium arsenate, and titrating with decinormal silver-nitrate solution till the precipitate has taken a just perceptible pink shade. Each cubic centimetre of the silver solution will indicate 0·146 per cent. of NaCl, but, when potassium chromate has been employed as indicator, 0·2 c.c. must be deducted for the quantity required to produce the coloration. Instead of the ordinary decinormal silver solution, it is convenient to employ a solution containing per litre 2·905 g. $AgNO_3$, which indicates per cubic centimetre 0·001 mg. NaCl.

If an analysis is to be made for sale, a somewhat more accurate process must be employed. Ten grammes are calcined in a porcelain dish with the addition of a little ammonium carbonate, and weighed again, by which operation the moisture and the free acid are found. The latter is estimated by itself in a fresh uncalcined sample in the same way as described above. The calcined sulphate is dissolved in water and filtered, the residue weighed, treated with hydrochloric acid, and the iron in the solution estimated. The separation of alumina, which only occurs in very small quantity, is hardly ever made. The portion insoluble in HCl is calculated as sand. In the filtrate the chloride can be estimated as above, and the lime by precipitating with ammonium oxalate. It is, however, preferable to omit the calcining, and to proceed in this manner:—The sample is dried at 100° C., weighed, dissolved in water, and the weight of the residue (sand and a little ferric oxide) estimated. In the solution, which is reduced to a definite volume, free acid, chlorine, lime (to be calculated as sulphate), iron, etc., are estimated separately. In this case there is no danger of expelling any HCl. At some English works 0·75 per cent. is always reckoned for silica and ferric oxide, the free acid and undecomposed NaCl estimated, and the remainder taken as Na_2SO_4. This calculation, however, neglects the lime, and is inaccurate, for even with common pan-salt there is often upwards of 1 per cent. of $CaSO_4$, and with rock-salt even more than that.

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[1] If litmus were employed as indicator, an error would be caused by ferric and aluminium salts.

De Koninck[1] employs the following plan. He dissolves 50 g. sulphate and filters into a litre flask; the residue is washed and ignited. The filtrate is made up to 1 litre; 300 c.c. of this are used for estimating the free acid by titrating with ammonia, the latter being added till ferric hydrate begins to precipitate; a little litmus is added and again standard sulphuric acid, till the liquid just turns reddish. Al_2O_3 and Fe_2O_3 are estimated by adding chlorine- or bromine-water to 200 c.c. of the solution, precipitating by NH_3, filtering, etc. In the filtrate the lime is estimated by ammonium oxalate, the precipitate is washed, ignited, converted into calcium sulphate by sulphuric acid, and weighed as such. Or all three may be estimated together, without filtering off Al_2O_3 and Fe_2O_3, in which case, after adding sulphuric acid and igniting again, Al_2O_3, Fe_2O_3, and $CaSO_4$ remain. Sodium chloride is estimated in 100 c.c., as usual, by standard silver nitrate with potassium chromate as indicator, the free acid having been neutralised by a solution of borax. De Koninck considers the estimation of moisture by heating to 100° C. inexact, because, on the one hand, at that temperature some water still remains, and, on the other hand, the bisulphate acts on the sodium chloride, and hydrochloric acid is given off. He therefore estimates the water indirectly by heating 2 g. of sulphate in a covered platinum crucible to fusion, at which point water, sulphuric acid, and hydrochloric acid escape [an addition of ammonium carbonate would be useful in this case], and deducts from the loss, first, the "free" sulphuric acid; secondly, for each 117 parts of common salt decomposed (estimated by dissolving and titrating the NaCl still present) he adds another 25 parts ($SO_4H_2 = 98$, $2\ HCl = 73$)—that is, to 1 NaCl 0·214.

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[1] *Revue Universelle*, **85**, 366; **89**, 394; *Chem. News*, **88**, 252.

Isbert and Venator[1] dissolve about 2 g. of the sample in a little hot water, add a little ammonia and ammonium carbonate, filter from the precipitate, redissolve the latter in HCl, precipitate as before, and wash with hot water; the volume of the filtrate, with all washings, need not exceed 100 c.c. The precipitate comprises insoluble matter, ferric oxide, alumina, calcium and magnesium carbonates. The solution contains all the sulphate, besides sodium chloride and the "free acid" as ammonium sulphate. It is evaporated in a platinum dish on the water-bath, with addition of a little sulphuric acid, and the residue is ignited till all ammonium salts are driven off, and weighed. By deducting from the weight that of the Na_2SO_4, corresponding to the NaCl found by titration in the original sample, we find the real Na_2SO_4 originally present.

Grossmann[2] dissolves 3·55 g. saltcake in a half-litre flask, adds 30 c.c. of a cold saturated solution of barium hydrate, fills to the mark and shakes up. Two hundred and fifty c.c. of the clear portion are placed in a flask, carbonic acid is passed through for ten minutes, and the liquid is boiled to decompose the barium bicarbonate. After cooling it is diluted to 500 c.c. and filtered. 250 c.c. of the filtrate (*i.e.*, one-quarter of the original quantity) is titrated with normal acid. The following reactions have taken place:—

1. $Na_2SO_4 + (x+1)Ba(OH)_2 = BaSO_4 + 2NaOH + xBa(OH)_2$.
2. $2NaOH + xBa(OH)_2 + (x+1)CO_2 = Na_2CO_3 + xBaCO_3 + H_2O$.

Hence the sodium carbonate ultimately found is equivalent to the sodium sulphate originally present. Corrections must be made for any barium nitrate contained in the hydrate and for the bulk of the precipitates, which renders the operation complicated and somewhat uncertain. In fact, Grossmann finds an inexplicable "constant error" of 1·3 per cent., which is added to the result obtained as above.

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[1] *Z. angew. Chem.*, 1890, p. 66.

[2] *Chem. News*, 41, 114.

Analysis of Acid Sulphate (Bisulphate, Nitre-cake).

Nitre-cake, that is, the residue from the manufacture of nitric acid, is a mixture of normal sodium sulphate and bisulphate in very varying proportions. For technical purposes it is usually only tested for "free" sulphuric acid—that is, for that present as bisulphate—in order to ascertain how much common salt it will take to neutralise this in the saltcake-pan (Chapter III.). This can be done with sufficient exactness by titrating a sample with standard caustic-soda solution without adding an indicator, until a yellow colour of a permanent precipitate is produced. It is also sometimes tested for *iron* and for *nitric acid* by means of the nitrometer (cf. *Nitric Acid* Volume); it ought not to contain more than traces of nitrate.

Those who desire for any reason to determine the sulphate in nitre-cake or saltcake may be interested in a rapid volumetric method for the determination of sulphates given by A. D. Mitchell and C. Smith.[1] The method consists essentially of adding a small excess of $N/5$ barium chloride solution, destroying mineral acid by sodium acetate, adding excess of $N/10$ ammonium bichromate solution, and making up to 100 c.c.; when the precipitate has settled, 25 c.c of the clear supernatant liquid are titrated with $N/20$ ferrous ammonium sulphate solution, using potassium ferricyanide as an external indicator. This has been applied to ammonium sulphate, potassium sulphate, zinc sulphate, magnesium sulphate, and copper ammonium sulphate, and gives results accurate to about 0·2 per cent., although in the case of potassium sulphate special precautions have to be adopted to minimise absorption. Excluding weighings, five determinations may easily be made in an hour.

Analysis of Hydrochloric Acid.

The *hydrogen chloride* in commercial muriatic acid is frequently ascertained merely by means of the hydrometer, with the help of the table of specific gravities (p. 44). We have already pointed out that the impurities of commercial muriatic acid frequently cause great errors in this mode of estimating its value, even when the specific gravity has been reduced to 15°, as must be done in every case. Hence frequently a direct estimation of HCl cannot be omitted. This can be sometimes done by titrating with standard soda solution, as has been described in the case of sulphuric acid (cf. *Sulphuric Acid*, Vol. I.). But this can only be done with muriatic acid nearly free from sulphuric acid, or in such cases where a moderate percentage of that acid is not of much consequence. Whenever these conditions are not present, the HCl must be directly estimated, either gravimetrically or, more expeditiously, volumetrically. For the latter purpose the acid must be neutralised with sodium carbonate, of which a slight excess does no harm, and, after adding a little yellow potassium chromate or sodium arsenate, the titration must be performed with decinormal silver nitrate, as described, p. 58. Errors in this estimation may be caused by the presence of chlorides of sodium, iron, or the like; but the sodium is hardly ever, and the iron very rarely, present in appreciable quantities. *Free chlorine* would also influence the above test; but it is very rarely present to any extent, and is then easily estimated by the methods described below. In the presence of nitrates the titration with potassium chromate does not yield quite accurate results, since silver chromate is soluble in nitrates.

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[1] *Chem. Soc. Proc.*, 1909, 25, 291.

A more accurate method for the determination of chloride in acid solution is by use of standard solutions of silver nitrate and potassium thiocyanate. No neutralisation is necessary, and the accuracy of the analysis is unaffected by the presence of iron or nitrates. For details of the procedure, see Cumming and Kay's *Quantitative Analysis*.

An electrolytic method of estimating hydrochloric acid is described by Goldbaum and Smith.[1]

Fuming hydrochloric acid is conveniently weighed in the "bulb tap pipette," described in *Sulphuric Acid*, Vol. I.

The ordinary *impurities* of hydrochloric acid may be detected and estimated in the following way:—

Frequently it contains *sulphurous acid*, arising from any hat may have been present in the sulphuric acid employed for reparing the hydrochloric acid, or from sulphuric acid acting pon iron or organic substances. The presence of sulphurous cid is most easily detected by means of sulphuretted hydrogen, with which it gives an opaque-white colour; for this reaction, however, Cl and Fe_2Cl_6, which may exist in very small quantities along with SO_2, must be absent. In the presence of SO_2, stannous chloride gives a yellowish precipitate of SnS_2.

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[1] *J. Amer. Chem. Soc.*, 1910, 32, 1468.

The quantitative estimation of SO_2 is made by titrating with iodine or potassium permanganate, but the presence of other impurities may cause errors. In this case the SO_2 is oxidised by one of the above-mentioned reagents, or by pure hydrogen peroxide. The H_2SO_4 thus formed is estimated by precipitation with $BaCl_2$, together with the H_2SO_4 originally present, and the latter is estimated in the same way in another sample before oxidation.

Sulphuric acid is one of the commonest impurities in crude muriatic acid; it is tested for and estimated by barium chloride. It must not be forgotten that $BaSO_4$ is soluble in a large excess of HCl, and that therefore such an excess must be neutralised by pure soda (not by ammonia!) or removed by evaporation. A rough estimation of the quantity of H_2SO_4 in crude muriatic acid can be made by comparing the opacity caused by $BaCl_2$ with that caused in acids containing a definite quantity of H_2SO_4. For some purposes muriatic acid should be entirely or almost entirely free from sulphuric acid—for instance, for revivifying the animal charcoal used in sugar-works. Muriatic acid for pickling iron previous to galvanising (coating with zinc) ought not to contain more than 1 per cent., or at most 1·5 per cent. of SO_3 (Rürup).

The above-mentioned "opacity" method has been developed by Rürup[1] into a somewhat more accurate process, sufficient for the ordinary checking of work, although not for the purpose of testing complaints made by buyers. He prepares small glass tubes, closed at the bottom, 6 mm. wide for a length of 250 mm., and then expanding into a small funnel; the top is adapted for closing with a cork. The narrow cylindrical part is provided with an empirical graduation in the following way:—A number of special acids are prepared by adding to 10 c.c. of pure hydrochloric acid as much sulphuric acid as corresponds to 0·4, 0·6, 0·8 per cent. SO_3, and so on up to 3·0 SO_3. These are heated to boiling, washed into the tubes, neutralised [illegible] sodium hydroxide, precipitated with hot

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[1] *Chem. Zeit.*, 1894, p. 225.

$BaCl_2$ solution, shaken for two minutes, and allowed to settle. A mark is made with a diamond at the level reached by the precipitate in the tube, indicating the percentage of SO_3. These tubes are employed in future tests by proceeding in a similar manner, *i.e.*, almost neutralising 10 c.c. of the acid by NH_3, adding 5 c.c. of saturated $BaCl_2$ solution, closing the tube with an indiarubber cork, shaking vigorously, and reading off the volume of precipitate after five minutes' settling. This method is also described by Jackson in *J. Amer. Chem. Soc.*, 1901, p. 799.

A rapid method of determining traces of sulphate is to precipitate in a Nessler tube and compare the opacity with that produced in various standard solutions, using the same volume of solutions and keeping all other conditions, such as temperature, time of standing, etc., constant. The method can be made more exact by placing a piece of paper on which small squares, about 3 mm. square, have been drawn in chess-board fashion, and finding how much of the solution and of the tandard solution must be used to obtain in each case sufficient recipitate to just mask the pattern when viewed through the olutions in Nessler tubes.

Free chlorine is frequently found in hydrochloric acid, specially if the sulphuric acid employed in the preparation f the latter contained nitrous acid. A starch solution containing otassium iodide is a good test for its presence; but it is ecessary first to add some pure HCl or H_2SO_4 to the reagent n order to ascertain whether it is coloured blue by acidifying lone, owing to the presence of iodate. Since even ferric hloride liberates iodine, it is better to heat the acid and to old a strip of iodide of potassium-starch paper in the vapour.

A very accurate method is the following:—The acid is laced in a flask, from which the air is completely expelled by stream of CO_2, and the acid is now shaken up with a strip of bsolutely clean copper-foil. In the presence of chlorine, copper dissolved, which can be detected by potassium ferrocyanide, tc. Le Roy[1] detects free chlorine by means of a solution of iphenylamine.

Bromide and *Iodide* may occur in hydrochloric acid as HBr nd HI, owing to their presence in the salt. They are tested for by adding a very little chlorine-water, and shaking up with chloroform, which dissolves bromine with a yellow, and iodine with a purple colour.

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[1] *Bull. Soc. Chim.* [3], ii., p. 279.

Ferric chloride is found on evaporation to dryness, along with any soda, lime, and other refractory substances carried over mechanically in the manufacture of sulphate, or contained in the water employed for condensation. According to Stas, even quite pure acid, which on evaporating in a platinum retort leaves no residue whatever, on evaporation in open vessels takes up matters floating in the air and leaves a yellow residue, frequently containing iron. The strongly yellow colour of crude muriatic acid is frequently not caused by iron, but by organic substances. The iron is detected by ammonium sulphide; potassium ferrocyanide, or potassium sulphocyanide; the latter two show it only when present as perchloride. Its estimation in the absence of alumina is made by precipitation with ammonia; in the presence of alumina by reducing with pure zinc, adding some phosphoric acid, and titrating with potassium permanganate. Titration with permanganate in presence of such large excess of hydrochloric acid is at best an unsatisfactory process and it is better to use standard dichromate. According to Venables[1] the iron present in hydrochloric acid is best detected by adding a concentrated solution of cobaltous nitrate, coloured blue by addition of concentrated hydrochloric acid; even traces of iron change the colour to green.

Arsenic frequently occurs in hydrochloric acid as $AsCl_3$, from the arsenic contained in the sulphuric acid. Houzeau found, on the average, 0·1 g. $AsCl_3$ in a kilogramme of commercial acid; Filhol and Lacassin, from 1·02 to 5·007 g. As_2O_3 (=0·8 to 4·28 As); Glénard, 2·5 g. As_2O_3; H. A. Smith, 6·91 g. As_2O_3 (=5·18 As); Hjelt (from the same raw material as Smith), in pan-acid of 36° Tw. 0·66, in roaster-acid of 32° Tw. 0·14 g. of arsenic per litre. Arsenic is tested for by Marsh's apparatus, by (Reinsch's test) blackening a strip of copper, or by giving a voluminous brown precipitate with stannous chloride (Bettendorf). If sulphurous acid and arsenic are to be simultaneously sought for, Hilger[2] adds iodine solution. Should this be decolorised, either SO_2 or As_2O_3 is present. More iodine solution is then added until an excess of it is present; the acid is poured into a test-tube, a few pieces of zinc are added, and the tube is loosely closed with a cork to which a strip of paper moistened with silver nitrate solution is attached. If any arsenic was present, AsH_3 is given off, and the paper is blackened; if not, the original acid is again tested for SO_2 by first precipitating the sulphuric acid with barium chloride then adding to the filtered liquid iodine solution till the colour is permanent, whereupon, if SO_2 was originally present, a new precipitate of $BaSO_4$ is formed.

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[1] *Fischer's Jahresber.*, 1887, p. 546.

[2] *Wagner's Jahresber.*, 1875, p. 445.

The German Pharmacopœia prescribes the following mode of performing this test:—Three c.c. of the hydrochloric acid are mixed with 6 c.c. of water, and placed in a test-tube 1¼ in. wide. An iodine solution is added till a faint yellow colour appears, then a few pieces of zinc; a loose plug of cotton-wool is introduced, and the tube is covered with a piece of filtering-paper, the centre of which contains a drop of concentrated solution of silver nitrate (1 : 2). If arsenic is absent, this spot should not exhibit any yellow colour, which turns black on moistening with water, either at once or after a quarter of an hour, nor should there be any brown shade, blackening towards the centre.

Another test for arsenic is the following:—A layer of sulphuretted hydrogen solution is carefully poured on to the acid; neither at the ordinary temperature nor on placing the tube in hot water (arsenic acid) should a yellow ring be formed round the area of contact within an hour. This test shows $\frac{1}{1000}$ per cent. of As in concentrated acid, but is not quite o sensitive with dilute acid.

Luckow[1] showed that by electrolysis arsenic is precipitated ith dark-brown or black colour and graphite-like lustre; it oes not dissolve in hydrochloric acid even on heating, but disolves in concentrated nitric acid and in sodium hypochlorite.

Ziegler[2] examines hydrochloric acid both for As and SO_2 y passing the hydrogen, produced by zinc, first into a very ilute ammoniacal solution of copper, which indicates the H_2S ormed from the SO_2, and then through a weak silver solution, hich decomposes the AsH_3.

Kretzschmar[3] estimates the arsenic in hydrochloric acid as follows:—The acid is diluted and is approximately neutralised with soda; to this are added ammonia and yellow ammonium sulphide, then an excess of pure hydrochloric acid; the liquid is placed on a water-bath, and H_2S is passed in. After two hours all the arsenic is precipitated as As_2S_3, which is washed, dissolved in caustic potash and bromine, and the arsenic precipitated from the slightly acid solution by ammonia and magnesium sulphate. The precipitate is thoroughly washed, dissolved on the filter in dilute nitric acid, the filtrate evaporated in a platinum capsule, and the magnesium pyroarsenate ignited at a red heat.

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[1] *Z. anal. Chem.*, 1880, p. 1.

[2] *Fischer's Jahresber.*, 1880, p. 328.

[3] *Chem. Zeit.*, 1891, p. 299.

For most purposes the following process will suffice:—The $AsCl_5$ in the acid is reduced by SO_2, then As_2S_3 is precipitated by H_2S, washed, dissolved in ammonia, the solution is evaporated in a thin glass or porcelain dish, the As_2S_3 dried at 100° and weighed. One part of As_2S_3 is = 0 6093 As or 0 80429 As_2O_3.

Blattner and Brasseur[1] employ the reaction found by Seybel and Wikander.[2] They employ the hydrochloric acid at a specific gravity of 1·16 to 1·18, and, if necessary, bring it up to this by adding sulphuric acid, sp. gr. 1·45. Of such acid they take 50 c c, add 5 c c of a 30-per-cent. solution of potassium iodide, agitate well, allow to stand for one minute, filter the arsenic trioxide on a cotton-wool or glass-wool filter, and rinse the vessel with concentrated hydrochloric acid containing 10 per cent. of a 30-per-cent. potassium iodide solution. Then they place the funnel with the filter on a 300 c.c. Erlenmeyer flask, dissolve the precipitate by means of water, add excess of sodium bicarbonate, and titrate with decinormal iodine solution.

Schröder[3] found in hydrochloric acid, sold by druggists as "pure," so much *organic substance* that it possessed a putrid smell and decolorised potassium permanganate even when strongly diluted. He believed that this acid had been obtained as a by-product in the manufacture of aniline colours.

R. F. Tarbell[4] converts the arsenic into hydrogen arsenide which is passed through a solution of iodine in gasoline, whereby it is converted into arsenic tri-iodide. Twenty-five g. of the acid are treated with 35 g. of zinc and 1 c.c. of stannous chloride solution (50 g. Sn per litre). The specific gravity of hydrochloric acid is first adjusted to about 1·1 and that of sulphuric acid to about 1·40 by addition of either water or arsenic-free acid. The reaction is allowed to proceed for about two hours, with warming if necessary; then 20 c.c. of sulphuric acid, of sp. gr. 1·4 are added, and the reaction allowed to continue for one hour more. The evolved gases are passed through a solution of lead acetate to remove hydrogen sulphide, and then through a bulb tube containing 80 c.c. of purified 60° gasoline, 20 c.c. of water, and 20 c.c. of a solution of iodine in purified gasoline (0·6773 g. per litre). (The gasoline is purified by washing twice with sulphuric acid, then with dilute sodium hydroxide and with water.) The contents of the bulb tube are subsequently shaken with 200 c.c. of sodium arsenite solution (0·264 g. arsenic trioxide, 1 g. sodium carbonate, and 1 g. sodium bicarbonate per litre), the aqueous layer removed, and the excess of arsenite titrated with iodine solution (0·6773 g. iodine and 1·2 g. potassium iodide per litre). The equations given are:—

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[1] *Chem. Zeit.*, 1904, p. 211.

[2] *Chem. Zeit.*, 1902, p. 50.

[3] *Chem. Zeit.*, 1885, p. 857.

[4] *J. Ind. Eng. Chem.*, 1914, 6, 400-401.

$$AsH_3 + 3I_2 = AsI_3 + 3HI;$$
$$2AsI_3 + 3H_2O = As_2O_3 + 6HI;$$
$$As_2O_3 + 2I_2 + 2H_2O = As_2O_5 + 4HI.$$

1 c.c. of the solution of iodine in gasoline is equivalent to 0·00005 g. arsenic.

H. Koelsch[1] describes the following rapid method for the determination of arsenic in hydrochloric acid. One hundred c.c. of hydrochloric acid are boiled with 200 c.c. of water and 5 c.c. of potassium iodide solution (50 g. per litre) until the liquid is only yellow or faint brown, then after addition of 5 c.c. of sodium sulphite solution (25 g. of crystalline salt per litre), boiling is continued for five minutes, the liquid diluted to about 700 c.c., made nearly neutral to methyl-orange with caustic alkali, treated with sodium bicarbonate, and titrated with N/10 iodine solution. Small amounts of nitric acid are negligible, but larger quantities and the presence of substances that react with iodine in alkaline solution render the method useless. For a gravimetric determination the diluted acid is treated with iodide and sulphite as described, and the reduced arsenic precipitated from the hot liquid by means of sodium sulphide solution (40 g. per litre). The precipitate is separated, dissolved in ammoniacal hydrogen peroxide, and the arsenic precipitated as magnesium ammonium arsenate. The results were in close agreement with those obtained by standard methods.

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[1] *Chem. Zeit.*, 1914, 38, 5.

Selenium occurs very frequently in hydrochloric acid, in consequence of seleniferous sulphuric acid being employed in its manufacture.[1] Divers[2] derives it from a selenium sulphoxide, dissolved in sulphuric acid:

$$2SeSO_3 + 2HCl = Se_2Cl_2 + H_2SO_4 + SO_2.$$

Selenium may cause errors in the Reinsch test for arsenic, as it stains the copper-foil similarly to arsenic; but if the foil is heated in a dry test-tube, a sublimate is formed which dissolves in sulphuric acid with a brownish-green colour.[3]

Dr Reidemeister, of the Schönebeck Chemical Works, (private communication) states that red-brown deposits of selenium (sometimes very pure) occur at times in roaster acid, but never in pan acid. It is found especially in the connecting pipe between the receivers.

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[1] *Cf.* Kienlen, *Bull. Soc. Chim.*, 1882, p. 40.

[2] *J. Soc. Chem. Ind.*, 1885, p. 33.

[3] *Fischer's Jahresber.*, 1884, p. 348.

CHAPTER III

THE MANUFACTURE OF SALTCAKE AND HYDROCHLORIC ACID FROM SULPHURIC ACID AND SALT

HYDROCHLORIC acid and saltcake are manufactured almost entirely from the raw products sulphuric acid and salt. The apparatus used depends largely on whether saltcake or hydrochloric acid is the more desired product, and is still curiously influenced by what was done locally in the past. The earliest reference I can find to a British Patent for the manufacture of either of these substances is in that granted to William Sidgewicke (No. 641) in 1749. The "spirit of salt" is made by distilling from an "earthern long neck" placed in a "reverberatory furnace" a mixture of 1½ lb. of ground and dried sea-salt and 4½ lb. of dry "powdered tobacco-pipe clay or Fuller's earth, or indeed any clay" mixed well together, having a capacious receiver; "the heat is increased gradually for ten hours that the long neck may be of a moderate red heat; continue this heat for five hours longer, by which time your operation will be finished."

Soon after this, the use of sulphuric acid was recognised as the best way for manufacturing hydrochloric acid from salt.

Manufacture in Glass Retorts.

This method is now only of historical interest, and those desiring any details are referred to earlier editions. The process had the advantage of yielding an acid almost free from iron, but suffered from several serious disadvantages. If the amount of sulphuric acid used was only sufficient to give the normal sulphate, the residue in the retorts broke them on cooling. If excess of sulphuric acid was used in order to obtain a fusible residue, there was great danger of getting the hydrochloric acid much contaminated with sulphuric acid. When the process was in use, it was customary to break up the retorts in order to obtain the saltcake, and the broken glass was then sent to a glass-works to be remelted.

Manufacture in Cast-Iron Retorts (Cylinders).

This was the type of plant often adopted when muriatic acid was the main product, but it has been steadily dropping out of use.

In France the cylinder-furnaces seem to have been given up some time ago;[1] but in London and several other places they exist even up to now, in order to supply a local demand for muriatic acid. In 1904 there were still 16 cylinder-furnaces at work in Great Britain, principally in South Lancashire, and about 1200 tons saltcake was made in that way. Such furnaces also still exist in the United States, and a few were still in use in England in 1919, so that a description may still be of some value.

The process admits of a larger scale of working than with glass retorts. Figs. 1 to 7 show such an arrangement. Two cylinders, A A, lie in a furnace, of which usually a large number are placed side by side B is the fireplace, C the partition-wall between, D the fire-arch; *e e* the escape-holes leading to the flues *f* and *g*, which open into a chimney common to all the furnaces. The back end of the cylinders is either closed by a cast-metal plate or by a wall of bricks with very narrow joints, set in mortar of 1 part of plastic clay and 1 part of burnt fireclay. [This latter arrangement will certainly not stand the action of the melting mass; a round flag of stone or of stoneware in *one* piece is undoubtedly preferable.] This end of the retort contains a stoneware pipe *a*; on this is put a stoneware junction *j*, shown on a larger scale in Fig. 5; and this leads to the receivers I. The joints are plastered either with clay or with gypsum. The receivers are singly connected with a second row of receivers by the pipes K; the second row communicates by the pipes L L; at the end of the row there is a junction-pipe, L′, for a third row of receivers, connected with a fourth row by the pipes L″ L″; a fifth and a sixth row (M N, O P) usually ultimately lead to the chimney H. This connection, however,

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[1] *Cf.* E. Kopp, in Wurtz's *Diction. de Chimie*, ii., p 1567.

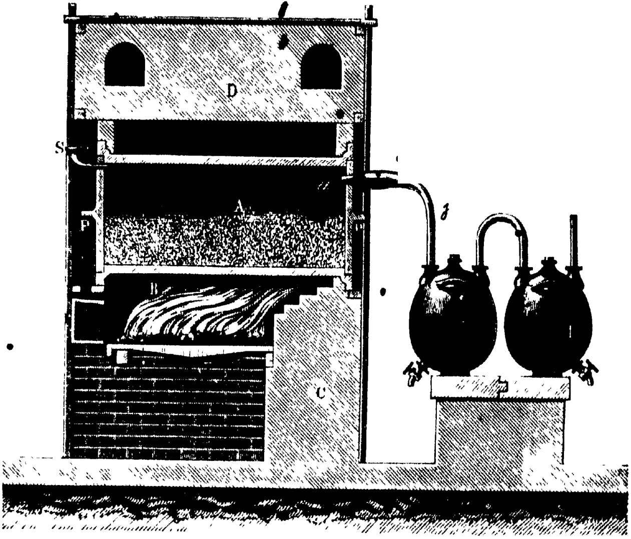
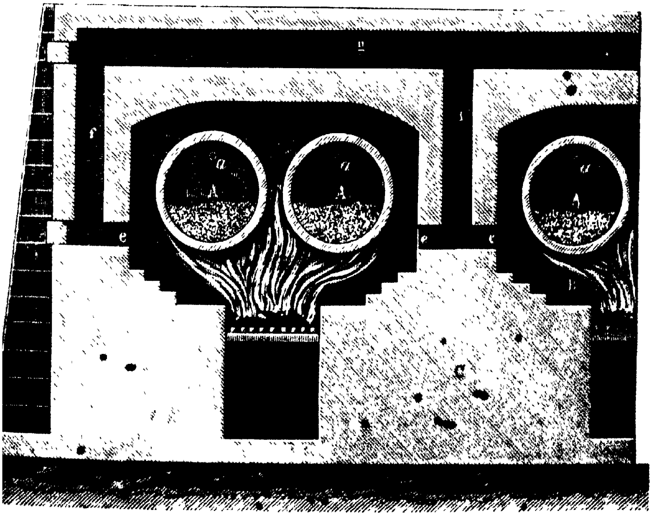


Fig. 1.



is bad; in the case of cylinders there is no necessity for producing an artificial draught in the apparatus, by which a large quantity of acid is carried away without condensation and creates a nuisance in the neighbourhood. The receivers should and must condense the acid gas so far that the gas can issue freely out of the last of them; otherwise no chimney, but a coke-tower, must be employed (see later).

The front end of the cylinders is closed for each operation by a cast-iron cover with handle P, a little clay making the joint tight; an opening, R, 2½ in. wide, receives the funnel-tube S for pouring in the acid, and is afterwards closed by a plug, S′.

The operation is carried on as follows:—The first row of receivers is left empty, the others are half-filled with water; the empty row receives the acid contaminated by sulphuric acid and sulphate carried over mechanically. The cylinders, which are 2 ft. 2 in. in diameter and 5 ft. 6 in. long, are charged with 160 kg. of salt, the cover is put on and luted; 128 kg. sulphuric acid of 144° Tw. is passed in through the funnel [this is considerably less than equivalent to the salt], the funnel taken out, and the stopper put in. The reaction commences at once, and is assisted by a small, gradually increasing fire. The metal cylinders can easily be heated sufficiently for the conversion of the common salt into neutral sulphate; and therefore no more than an equivalent of sulphuric acid is employed, usually even less, because it is dearer than the salt, and its loss of more consequence The more dilute the sulphuric acid the more it acts upon the iron, and therefore it ought never to be below 152° Tw.; it will then evolve a good deal of muriatic acid while still cold, and the fire need only be applied later.

The hydrochloric acid given off is condensed in Woulfe's bottles. Sometimes each of them has a tap, T (Fig. 6), of its own, but this is not necessary, and it has become quite usual to connect the bottles with one another by rubber tubes or, still better, by overflow-pipes taking the acid from the bottom of one bottle to the middle of the next one, as we shall see later.

In any case the gas travels in the direction K L L′ L″ M N O—that is, from the cylinders towards the chimney, whilst the water travels in the opposite direction, 1, 2, 3, 4; so that fresh

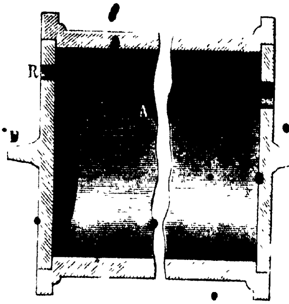


FIG. 3.

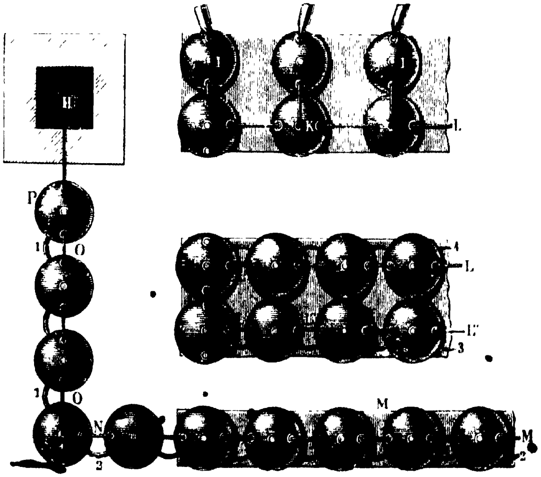


FIG. 4.

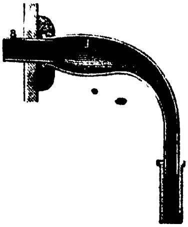


FIG. 5.

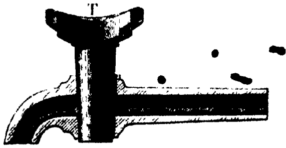


FIG. 6.

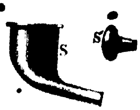


FIG. 7.

water meets the gas almost free from acid, and the weak acid formed in this way is concentrated in the first rows of receivers by stronger gas. Altogether about 200 to 208 kg. of muriatic acid with about 40 per cent. [?] of dry HCl, showing 21° to 22° Baumé, are said to be obtained from the 160 kg. of salt.

The completion of the operation is recognised by the gas-pipe becoming cold. The firing is then stopped, and the front cover is taken off by means of a hook put through the opening R. [There ought to be in any case, though Payen does not mention it, a set of pulleys, or at least a pulley provided with a chain and hook so arranged that it travels easily in front of each retort.] Then the saltcake, weighing 180 to 184 kg. is raked out in one or two pieces. This is never pure sulphate, but either contains bisulphate, or, where the muriatic acid is the main thing, undecomposed salt; it can only be used for very common bottle-glass, and is therefore mostly worked up in alkali-works into good saltcake. It is usually called "cylinder-cake."

According to Dreyfus (B. P. 13827, of 1896), the cylinder furnaces are worked at a partial vacuum, at a temperature not exceeding 260° C. His apparatus is arranged exactly like Valentiner's nitric-acid apparatus.

Manufacture in Furnaces.

This is the method by which saltcake has always been made on a large scale, from the time when it was the principal product and muriatic acid only a by-product, formerly often a very troublesome one.

The saltcake furnaces, unlike the glass apparatus and the iron retorts described above, always consist of two parts (except most of the mechanical furnaces), viz.:—one, consisting of cast-iron or lead, in which the first stage of decomposition takes place at a lower temperature—the *decomposing-pan* or *pot*; and another, consisting of brickwork, in which the decomposition is completed at a higher temperature—the *roaster* or *drier*. Formerly the whole operation was sometimes carried out from beginning to end on the dished hearth of an open roaster, all hydrochloric acid escaping into the chimney along with the fire-gas, but this barbarous style of manufacture will not be described here at all. The *pan* in all cases is heated from the outside, although in some cases a further heating from the top is added. The *furnace*, however, is either an ordinary reverberatory furnace or open roaster, or it is heated partly by the direct flame and partly indirectly through the bottom (gas-furnaces), or entirely by indirect heat (muffle-furnaces or blind roasters).

The principal matters to be attended to in constructing a furnace are the following:—

(1) *The Condensation of Hydrochloric Acid.*—The construction of the decomposing apparatus varies according to whether the object be that of obtaining the strongest acid for sale, or moderately strong acid for consumption within the works, or only weak acid for running away. Only in the last case, where nothing but very weak acid need be got, can pans worked by an open fire be employed; where acid is to be used as it is made, the calciner may be either a close or an open roaster; but where sale-acid has to be made, close roasters are nearly always preferred. The reason for this difference is quite obvious, viz., that the muriatic acid can be made all the stronger in the condensing-apparatus, the less it is mixed with air and fire-gas.

(2) *Turning out large quantities*, with the largest possible saving of time and wages. In smaller works contrivances may be used which are out of place in large works, where very large quantities have to be turned out, and *vice versa*. Thus, for instance, more work can be done with open roasters than with close ones, and most of all with furnaces where the pans are equally heated from above by the open flame, though in the latter case only weak acid can be obtained. The heating of the pan by the waste heat of the roaster is also, at least in England, principally confined to smaller works; in larger works this is not always done, because it makes one part of the apparatus dependent upon the other, so that one must frequently wait for the other, and nothing like as much work can be turned out in the same time as with separate fires. The extent of production, of course, must also determine the size of the furnaces and pans and even the material of the latter. In cast-iron pans much more work can be done than in lead pans, because the former can be used much more roughly and fired more intensely. The largest production is possible in the mechanical furnaces.

(3) *The Consumption of Fuel.*—Where fuel is dear and wages low, opposite considerations prevail to those stated just now for large production. The furnaces are then constructed so as to consume as little fuel as possible; the pan is always heated by the waste fire of the roaster, sometimes even both were heated by the waste heat of a black-ash furnace, but with the result that much less work could be done in a furnace during a given time.

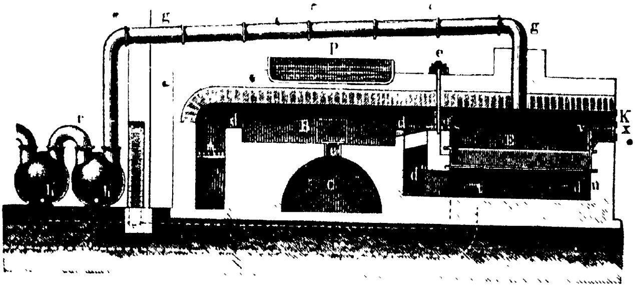


FIG. 8.

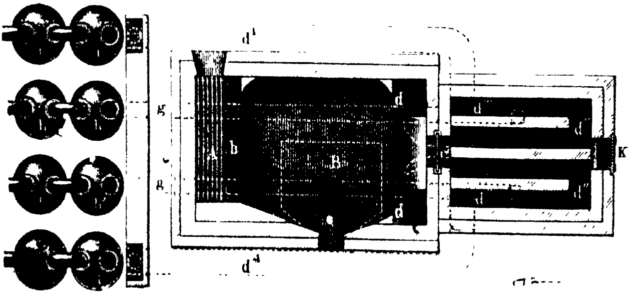


FIG. 9.

(4) *The Purity of the Saltcake.*—Where the object is that of making saltcake for glass-works, as free from iron as possible, lead pans as prescribed by Leblanc are still used. Thus in Belgium, for instance, sulphate of soda is made containing only 0·007 per cent. of iron. Where, however, the purity of the saltcake is not so material, as for alkali-making, lead pans have been almost everywhere supplanted by cast-iron ones, first introduced in the year 1839, when J. C. Gamble took out a

patent for cast-iron saltcake pans. H. Lee, at Felling-on-Tyne, had at the same time made the same invention. The lead pans are usually oblong with a slanting side for pulling out the saltcake; the metal pans sometimes, but rarely, have the same shape; they are nearly always shallow dishes in the shape of a segment of a sphere cast very thick; they will be described in detail further on.

Saltcake Furnaces with Lead Pans.

The oldest saltcake furnaces with open roasters were those constructed by Leblanc, and known in France as *bastringues.* They are represented in Figs. 8 and 9. They are described in detail in the first edition of this work, Vol. II., pp. 52 to 56, to which the reader is referred, as the bastringues are now quite obsolete. The same holds good of the Belgian calcining-furnace with two pans, shown and described in the same volume, pp. 56 to 60.

Much better are those furnaces introduced later on in Belgium and elsewhere, which combine lead pans with *muffle*-shaped calcining furnaces. Instead of describing the furnace, which was figured in the Belgian Blue-book of 1855, and and which has been copied into some technical works, a more recent construction is shown which was actually at work in Belgium, and is here represented in a sectional elevation and two sectional plans (Figs. 10 to 12). A is the fireplace, B the muffle; the flame passes between the muffle-arch *a* and the top arch *b*, which is made double, and contains an air-space, *c*, to lessen radiation. The air-channels *d d*, opening outside, serve for cooling and protecting the adjacent parts of the furnace. The flame descends in the flues *e e*, and passes through *f f* underneath the bottom, *g*, of the muffle; the latter is made specially strong near the fire end, on account of the danger of fluxing, and also at the back end. The openings *h h* serve for cleaning out the flues, and are usually closed. From the bottom of the muffle the fire either passes through *i* directly to the chimney, or first underneath the lead pans C C, the dampers *k k* permitting precise regulation. The plan Fig. 11 shows very well how the pans are supported from below. The pans are ¾ in. thick, and stand on cast-iron plates, preferably double ones

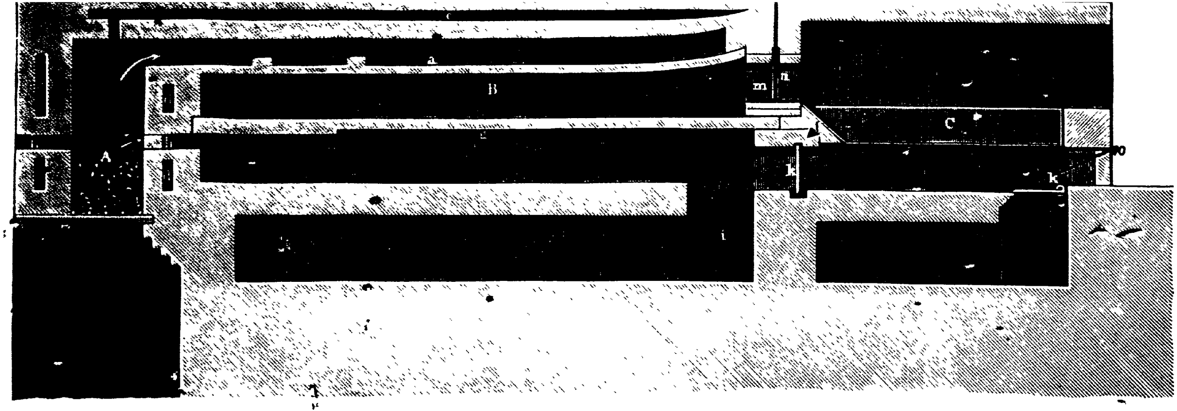
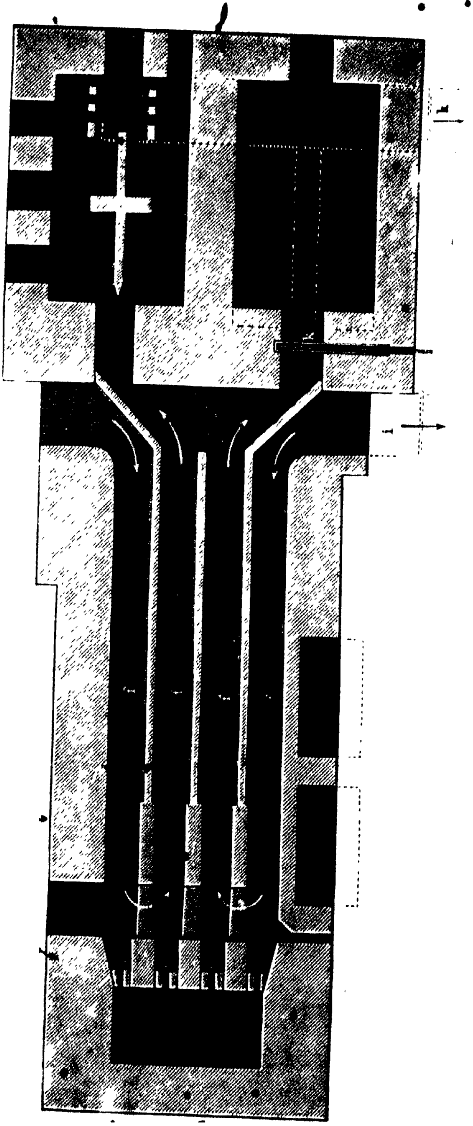


FIG. 10.



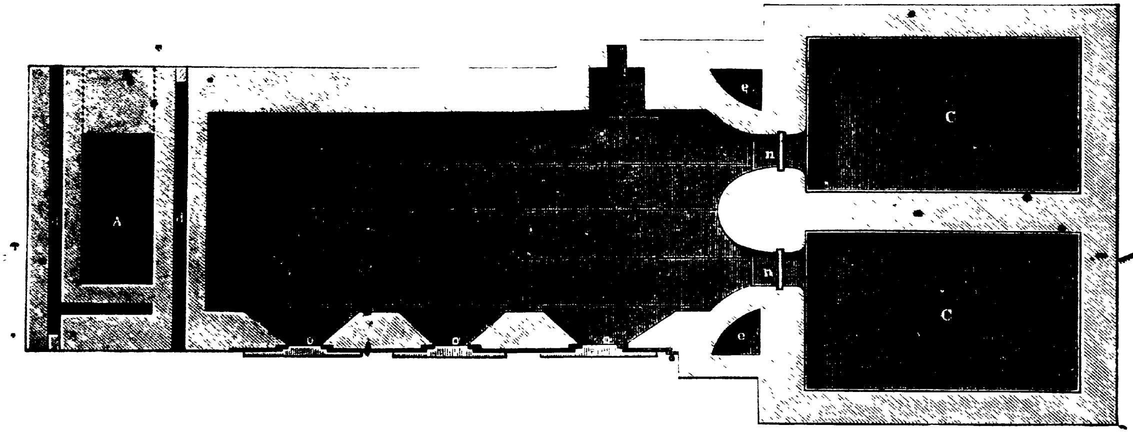


FIG. 12.

with 2 in. air-space between to prevent the lead melting. Small holes can be repaired *in situ;* and one pan may be working while the other is under repair. The air-channel *l* serves for cooling. The side of the pan next to the furnace slants upwards, so as to facilitate pushing the charge through the gangway *m* into the roaster B. The damper *n* is usually shut, as the muffle-gas is strong enough to admit of being mixed with the pan-gas, but if muriatic acid free from sulphuric acid has to be made, the pan-gas must be separated from the roaster-gas by the damper *n.* The finished saltcake is drawn from the working doors *o o* into boxes, in which it is wheeled away to the warehouses.

This furnace can put out as much as 5 tons of saltcake in twenty-four hours Its exact dimensions are: total length 39 ft.; outside width of the roaster 11 ft. 2 in., of the pan-furnaces 16 ft. 5 in.; grate 2 ft. 7½ in. wide, 5 ft. 11 in. long; height of the firebridge above the grates 5 ft. 11 in.; thickness of the side walls of the fireplace 2 ft., air-channels 4 in. wide; depth of the flue on the top of the muffle 12 in ; thickness of the upper arch 1 ft. 7½ in. (inclusive of a 5-in. air-course in the middle), of the muffle-arch 4 in., with a few strengthening ribs as shown in the diagram; thickness of the muffle-bottom 3 in., but in front and at the back 8 in.; inside length of the muffle 19 ft. 6 in., width 7 ft. 10½ in., up to the working-doors 9 ft. 2 in.; height up to the spring of the arch 8½ in., up to its crown 1 ft. 10 in.; gangway between the muffle and the pans 1 ft. 9 in. high, 1 ft. 4 in. wide; flue underneath the muffle 2 ft. 3½ in. in the middle; flues underneath the pans 1 ft. 7½ in. high; communication between the flue underneath the muffle and those underneath the pans [illegible] ft. 7½ in. square; pans ¾ in. thick, 7 ft. 10½ in. long at the bottom, 9 ft. 2 in. at the top, 5 ft. 11 in. wide, 1 ft. 5 in. deep.

The employment of a blind roaster is not indispensable for obtaining saltcake sufficiently pure for glass-making, especially with a deep fireplace as here designed and with moderate draught; it has been made compulsory in Belgium merely for the better condensation of the muriatic acid. We shall see below what rules have to be observed in this respect in the construction of blind roasters.

In a factory where saltcake was made exclusively for glass-works, Lunge observed the following mode of work:—The decomposition of the salt takes place in comparatively very small lead pans; this admits of regulating it very accurately, and driving the reaction in the pan up to 75 per cent., so that the mass, on being moved over into the roaster (which in this case is a reverberatory furnace, fired with coke), instantly solidifies.

Saltcake Furnaces with Cast-iron Pans (Pots).

Much more widely used than decomposing-furnaces with lead pans are those with *cast-iron pans*, now employed wherever saltcake is made for the manufacture of alkali. According to Henry Deacon,[1] the first inventor of the present decomposing-pans was J. C. Gamble, who, on 14th March 1839, patented a kind of rectangular flat-bottomed retort. Directly after, H. Lee, having opposed and defeated Gamble's patent, introduced a pan, shaped like a large cast-iron spoon, whose broader side was turned towards the workman, the smaller side towards the roaster. Gamble then introduced a round "pot," smaller and deeper than the present shape, and placed in an outer pan for protection. From this the present shallow uncovered pan, directly exposed to the fire, has been developed.

In some rare cases the form of the pan resembles that of the lead pans just described; and they are then heated by the waste fire of the roaster, precisely in the same manner. Mostly, however, they are shallow cast-iron dishes, 9 to 11 ft. in diameter, and 1 ft. 9 in. to 2 ft. 6 in. deep; their thickness varies from 5 to 7 in. in the centre, and from 2 to 3 in. near the edge; their weight is from 5 to 6½ tons. Their edge is either quite even (Fig. 13), or provided with a plain horizontal flange (Fig. 14), or with an upstanding margin on a horizontal flange (Figs. 15 and 16). These forms differ, especially in respect of the boiling-over of the mass and the escape of acid vapour. At the present time (1922) all the above types of pan are still in use, according to local preference. Possibly the favourite is that shown in Fig. 17, with dimensions suitable for a charge of [illegible] ton. The cover is very frequently formed by an arch independent of the pan, so that the latter, if cracked, can be taken out without any loss of time and replaced by a new one. Only the front wall of the pan furnace above the fireplace need be taken away and rebuilt; and the exchange is all the easier, as the pan, for other practical reasons, is

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[1] *Chem. News*, **28**, 163.

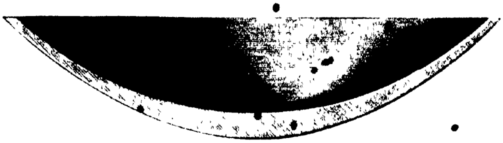

Fig. 13.

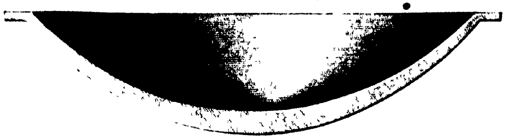

Fig. 14.

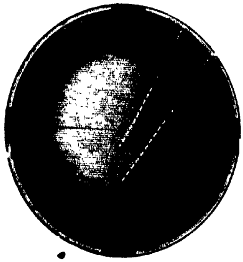

Fig. 15.

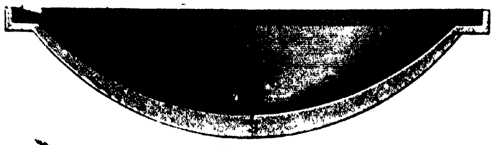

Fig. 16.

always set so that the bottom is nearly on a level with the ground, and the fireplace is built underground: this is done in order to have the working-door of the pan just at the proper working height, say 2 ft. to 2 ft. 6 in. above the ground. In

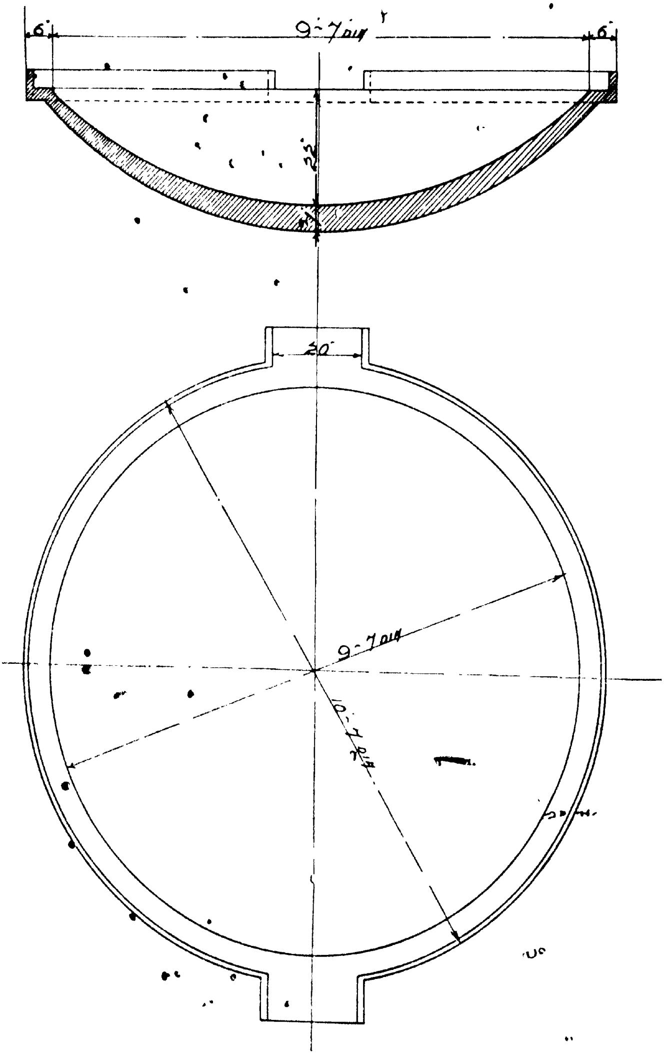

FIG. 17.—Standard Cast-iron Decco Pan.

laying out the decomposing-house, care should be taken that sufficient free space remains in front of the pan-furnaces, so that the pan can be pulled out by means of a winch and a new pan can be run in, for which purpose, as no work is going on, all the furnacemen, etc., will be available.

The pans usually have one or two lugs cast on, into which the chain of the winch is fastened. The new pan is placed on a strong wooden or iron bogie and run with this underneath the pan-arch, the bogie-wheels sliding on loose, flat, iron bars; the old pan is likewise run out on a bogie, or directly on the flat bars, previously greased with wagon-grease. At larger works there is always a pan ready on a bogie, or at least supported in such a way that a bogie can be run underneath and no time be lost. With energetic work no more than twelve to fifteen hours need elapse between the beginning of pulling down the brickwork of the old pan and finishing that of the new pan. At some works where all the pans are set in a single row, a railway runs parallel with them, which serves partly for taking away the saltcake, and partly for taking out cracked pans and putting in new ones with the assistance of a travelling crane.

In the case just described the pan can be kept in use a good deal longer than usual, if turned 90° every three months, so that fresh surfaces are always offered to the wear and tear in the worst places; pans can thus be made to last for eighteen months.

It is not quite so convenient if the arch is not independent of the pan, but rests upon the edge of the latter, as in Fig. 16. Figs. 20 to 23 (pp. 96-[illegible]) show this arrangement. In other cases such pans are built with a straight cylindrical wall, resting on the pan-edge and covered by a horizontal circular metal plate. In this case, when the pan cracks, the top arch, etc., must be taken down and rebuilt after putting in the new pan; this causes twelve to sixteen hours' detention, in addition to the time stated for resetting the pan with independent arch. The stoneware pipes for the acid gas, starting from the centre of the pan-arch, must be carried in the timber of the roof in such a way that they need not be taken away when the arch is pulled down: there is no question of this where the pipes are placed sideways.

The reason why such an arrangement has been preferred at many works, although the pan-arch has to be rebuilt every time, and time and wages are thus lost, is that only in this way can an escape of acid vapours into the chimney be with certainty prevented. With the ordinary pans (Figs. 13 or 14) standing loosely within an arch and either just touching it with their edges or connected with it by a low wall, it is very likely to happen that, or the contents of the pan boiling over (which cannot always be prevented), the acid will partly destroy the brickwork and open a slight communication between the space above the pan and that below it (viz., the fireplace). By the expansion and contraction resulting from great changes of temperature, the pan is already loosened and is easily detached from the arch, so that cracks and other communications of the kind just mentioned are formed. But since the draught of the chimney serving the fireplace is necessarily much stronger than that of the condensing-apparatus, which is in connection with the space above the pan, a good deal of the gas given off from the pan will inevitably be drawn downwards into the fireplace and thus escape directly into the chimney, as soon as the least communication exists between the space above and that below the pan. The smallest hole suffices for this; and it may last a long time, and much nuisance and damage may have been caused by the escape of hydrochloric gas before it is even noticed. This drawback is thoroughly prevented by the arrangement of resting the arch on the pan-edge itself, if the latter is bent upwards and visible outside, as shown in Figs. 16 and 20; for even if a hole is made in the pan by any acid boiling over, which cannot happen so easily on account of the turned-up flange, the gas issuing from it must escape into the working-space itself and must be noticed directly; in no case can it get into the fireplace. This drawback is not so likely to occur in the case of "plus-pressure furnaces" (see later on), so that the simpler forms of pans may be used with these furnaces.

In order to avoid the boiling-over of the contents of the pan, and the awkward consequences thereof, sometimes a cast-iron ring, 10 in. high, is cemented on to the top of the pan. This allows the arch to be kept separate from the pan, and is practically sufficient, as the contents of the pan never rise to the top of the ring.

An arrangement figured in Muspratt's *Chemistry* (iii., p. 908), and copied into many text-books, is also greatly recommended in Hofmann's *Report by the Juries* (1862). It seems to be obsolete now in England, but was observed by Lunge in a German works some years ago. It consists in providing the pans with sheet-iron dome-shaped covers, bricked over; the flame of the fireplace first travels over these covers, and then underneath the pan-bottom. The whole is a closed iron muffle, only provided with openings for charging, shoving, and carrying off the gas This construction is costly and complicated; it makes the renewal of a pan more troublesome, and facilitates the escape of acid vapours by any hole in the iron dome; the heating from above does no good, except indirectly by keeping the direct flame off the pan-bottom, which can be easily done in any case by proper setting, as we shall see below. In fact, at the German works where this style of cover has been adopted, the fire first goes underneath the pan-bottom and then over the top, where its only use is to protect the dome from being acted upon by the acid vapour, by keeping it hot. The arrangement drawn by Muspratt has never been general in Lancashire, as erroneously reported by Hofmann; it was only adopted at a few works, and seems to have been given up everywhere for many years past. Another arrangement (not to be confounded with this, and still found at some Lancashire works) consists of cast-iron domes for the pans, without any fire passing over them; they stand in the place of pan-arches; and on the occasion of renewing a pan its dome can be pulled up and let down again. Sometimes they are covered with bricks to keep them hot, and thus protect them from the acid vapours.

The *material* ~~of the~~ pan is of the greatest importance for its durability. It should be considered what demands are made on such a casting. It is expected to stand, without cracking, frequently repeated changes of temperature between the cold salt and acid, heated at most to 100° C., and the low red heat required by the reaction on the other hand. It must even stand, to a certain extent, the caking-on of crusts and the great local superheating consequent upon this, notwithstanding the great thickness which is given to it for the sake of durability. It has further to resist the attack of the fire from below and the much worse attack of the hot acids and the fusing bisulphate from above. In fact, even under the most favourable conditions, it can do this only for a certain time: a pan is considered to have done good service indeed if it works nine months and turns out 2500 tons of saltcake. Sometimes they last longer—up to 4000 tons, but mostly much less; and now and then they crack after a few days' use. In order to stand at all, they must consist of a mixture of several brands of pig-iron (kept secret by the founders), and must be cast with the greatest care. Pure charcoal pig, for instance, resists cracking by changes of temperature better than coke pig, but it is too soft and too easily attacked by acids.

It will be useful to remember in this connection Lunge's experiments on the action of sulphuric acid on various mixtures of cast-metal (*Sulphuric Acid*). Fohr[1] justly blames iron-founders for making vessels intended to treat acids and alkalis, viz., saltcake pans and caustic pots, from the same mixture of pig-iron. Those which have to resist acids should be rich in chemically combined carbon, with little graphite, much manganese, and little silicon. The metal ought to be tested by putting a sample in fused bisulphate of potash; 5·6 g. of metal with 27·2 g. of $KHSO_4$ should not lose above 25 per cent. of its weight. The pans are of course cast in loam—not in brick-out pits, however, but in cast-iron moulds thickly lined with loam, placed bottom upwards and provided with many holes for the escape of gas; a feeding-head of 9 in diameter and 2 ft. height produces a dense casting, any blowhole, of course, making the pan useless. In England the casting of decomposing-pans was formerly a monopoly of Messrs R. Daglish & Co., of St Helens, and the Widnes Foundry Company, of Widnes; for a number of years past several other foundries have also successfully taken up this work, as Messrs John Abbot & Co., of Gateshead, William Black, of South Shields, John Varley & Co., St Helens, etc. On the Continent, the decomposing-pans must generally be taken from the nearest foundry at which they can be obtained; the alkali-works are therefore nearly always compelled to abstain from heating them directly, and to employ merely the waste heat of the roaster; so that their whole style of working is different. There the pans rarely last, on an average, above 1500 tons of saltcake. They will last longer if the mixture is conveyed from them into the calcining-furnace in a thinner state.

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[1] *Fischer's Jahresber.*, 1886, p. 295.

According to a German patent of the Grusonwerk, Madgeburg (No. 45121), saltcake pans are made with a fireproof bottom, as shown in Fig. 18. The bottom is cast with outside ribs, of a dove-tail section, and the spaces between them are filled up with fireclay. Several alkali-works are stated to use these pans. [The diagram supplied from the Grusonwerk seems to refer to a caustic pot. This will, however, make no difference in the principle.]

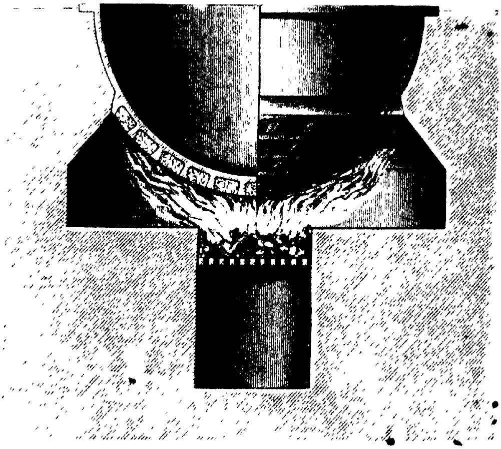

FIG. 18.

Blugel (Ger. P. 4207) proposed making saltcake pans entirely from brickwork, but this, of course, did not turn out a success.

It is hardly necessary to mention that the way of *setting the pans* (which will be described in detail later), and especially also the *treatment* of the pans, have very much to do with their durability, and that only very reliable and skilled men should be employed upon them. If the workman allows thick crusts to cake to his pan and, perhaps, pushes them off again suddenly, or if he allows the pan to become red hot towards the finish of the operation, and then at once charges it again with cold salt and acid, and so forth, the best pan may be cracked. *This is at once perceived through melted bisulphate getting into the fire-*

place; and in this case it is the rule in the best works to stop the work *at once* and to replace the cracked pan by a new one. It is often possible to work on a few days with a cracked pan, but with great loss of saltcake and gas. It is practically impossible to patch it, for riveting, cementing, etc., do no good, as has been proved by innumerable attempts.

The lower portions of the pan-setting, such as the fireplace itself, the arch over the same, the annular wall carrying the pan-edge, etc., are touched as little as possible on resetting a pan, unless they require repairing at the same time. The *fireplace* must, in any case, be constructed so as to avoid overheating parts of the pan-bottom, by which it would be most readily cracked. That this happens through unequal heating of single places can be perceived on cleaning out a cracked pan, when some places will appear more brightly red hot than the remainder. Frequently this can be remedied by enlarging or narrowing one or more of the "snore-holes" an inch or two; and the practised eye of a skilled furnace-builder must here frequently supplement the drawings. In order to avoid the damaging action of the direct flame, the firegrate is either placed very much below the pan, or a perforated (pigeon-holed) arch is placed between, as shown in the diagrams.

On the Continent it is the almost universal custom to heat the decomposing-pans by the waste fire of the muffle-furnaces. This not merely effects a saving of fuel, but it also almost entirely prevents cracking of the pans by an excess of heat, and admits of employing an inferior kind of casting, which, however, will tell on the life of the pans. In England the same arrangement is frequently found in some of the best managed works, but in many others it is preferred to heat the pans by a separate fire, which makes them independent of the work of the roasters and admits of getting through a maximum of work. This, of course, refers to muffle-furnaces (blind roasters). Open roasters should always be provided with separately fired pans. A very good arrangement is this: ordinarily the pan is heated by the waste fire of the muffle, but whenever the pan is under repair the furnace-fire can be sent directly to the chimney by a separate flue.

At some alkali-works the sulphuric acid, which is conveyed direct from the sulphuric acid works in a lead tube, arrives sufficiently hot, for instance from the Glover-tower or from a tank where tower-acid and chamber-acid are mixed. But where this is not the case, there ought always to be a special small pan provided for *heating the sulphuric acid*, made of cast-iron lined with lead, or of acid-proof stoneware, heated by the waste-heat of the pan-fire or by a steam-pipe, and at the same time serving for measuring off the acid required for each operation. It is for this purpose furnished with a glass float or with a fixed leaden scale. The outflow of the acid from the measuring-box into the pan is produced by a perpetually filled siphon, for instance, one like Fig. 19. The sulphuric acid in this small pan is heated up to 80° or 100° C.; without this preheating it is much more difficult to keep the decomposing pan from cracking.

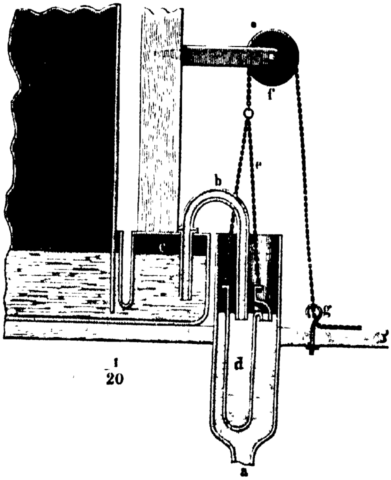

FIG. 19.

The *running-in of the acid* into the pan has also to be carefully attended to. If there is sufficient fall at disposal, the acid ought always to be run in at the top, in the centre of the pan-arch or close to it; for this purpose there is usually a short cast-iron pipe provided, firmly connected on the outside with the lead pipe conveying the acid from the measuring-box, and

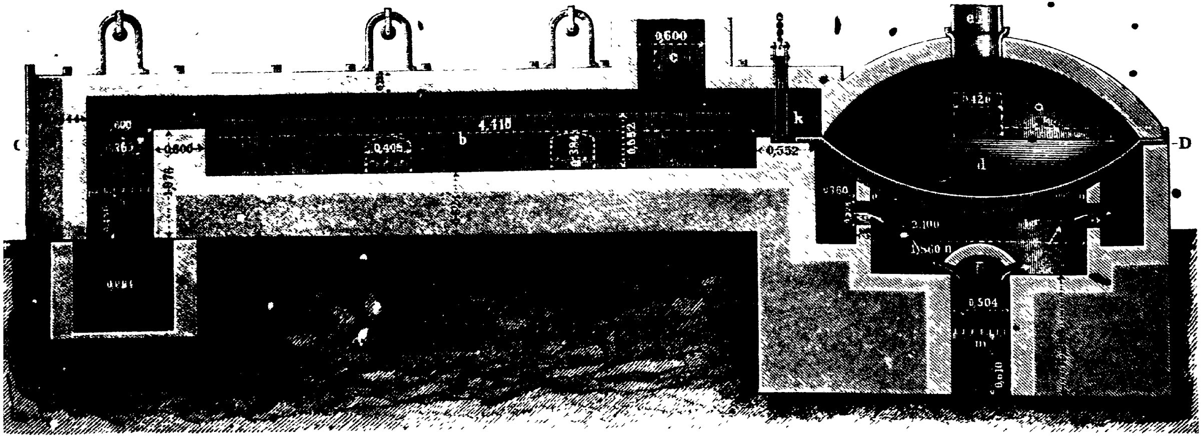
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FIG. 20.

frequently ending inside with a rose for scattering the acid in a fine spray. In this case the acid always runs on to the salt previously thrown in, without coming into immediate contact with the pan, and the cast-iron pipe itself lasts a considerable time, because it becomes hot and no acid can ever lodge in it. If, however, the measuring-vessel has to be placed lower down and the acid must be run into the pan sideways, this must never be done along the edge of the pan, because thus a channel will soon be formed in this place, and a crack will be the consequence. In this case the lead pipe must be put into a cast-iron one, projecting pretty far into the pan, so that the acid may get to the salt itself without running down the pan. This pipe will not last long, but it saves the pan. Stoneware pipes, etc., cannot be employed, even if they would stand the changes of temperature, because the men too often push their tools against them and thus break them

Saltcake Pans combined with Reverberatory Furnaces (Open Roasters).

In the first edition of this work, p. 72, a combination of a pan with two reverberatory furnaces is shown, where, as all the acid vapours were mixed with fire-gas, only hydrochloric acid of 4° to 6 Tw. could be condensed, which was partly used for bicarbonate, but mostly run to waste. Such pans with the roaster-fire heating them from the top were even then only exceptionally met with. Now that muriatic acid forms an essential economic factor at saltcake works, such an arrangement is simply impossible.

Much better is the combination where the pan-gas, and the gas from a reverberatory furnace are taken away separately. Such a construction, which has in practice proved entirely successful, is represented in Figs. 20 to 23.

The diagrams will be understood without much explanation (all the dimensions are marked in metric measure). Fig. 20 is a sectional elevation through the line A B of the plan; Fig. 21 a sectional elevation through the line C D of the preceding figure; Fig. 22 an outside elevation; Fig. 23 a sectional elevation through the line E F of the plan. The pan in this case is provided with a flange and upturned edge and a dome-

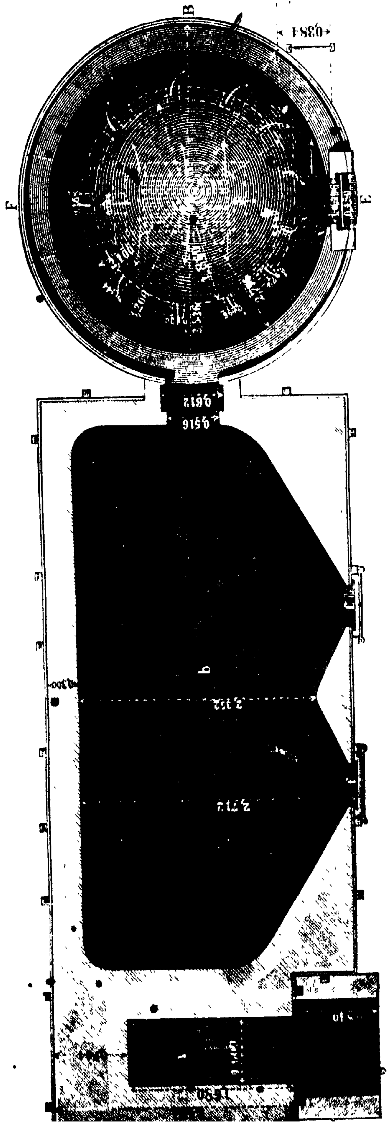

FIG. 21.

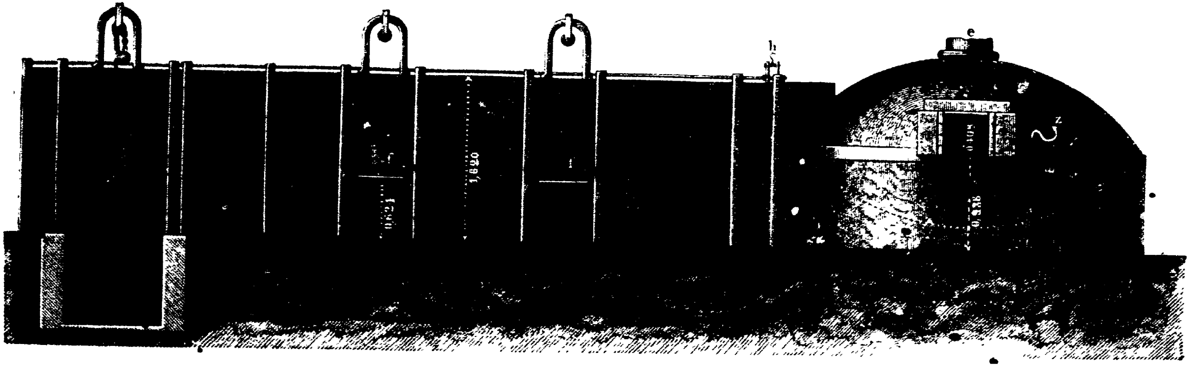

FIG. 22.

shaped roof, which has to be taken down and built up every time a new pan has to be put in. This, however, only takes a few hours, and the arrangement affords absolute security against any escape of hydrochloric-acid gas from the pan into the chimney.

The fire of the roaster travels from the grate *a*, through the roaster *b*, into the flue *c*, and then into the condenser for roaster-acid; the gas of the pan *d* goes independently through *e* into the pan-condensers. The roaster has two working-holes, *f f*,

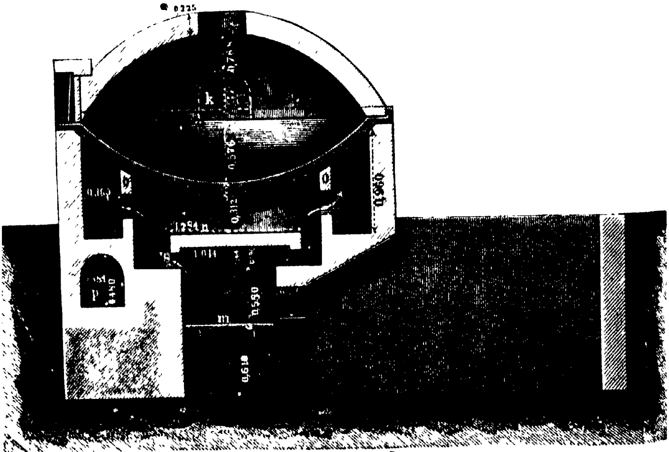

FIG. 23.

with bars for supporting the tools, and with doors made of a fire-clay tile in an iron frame, balanced by a chain, pulley, and weight, as shown at *g*. *h* is a balanced double damper of cast-iron, running in a groove of the gangway between pan and roaster, and luted with salt. Such double dampers, kept asunder by stay-bolts, are preferred, because single dampers are very quickly worn out at the edges by the acid vapours, and then allow the pan-gas from *d* partly to escape into the better-drawing calciner *b*; since the space between the two damper-plates is filled with salt, it is kept sufficiently gas-tight. The flange of the pan is interrupted at *i* and *k* for the charging-door and the shoving-hole. *l* is the funnel for the sulphuric acid, which, if there is sufficient fall, is better placed near the centre of the arch, so that the acid will run into the middle of the pan on to the salt; otherwise, as mentioned above, a cast-iron pipe (quickly wearing out) has to be used. The diagrams show how the fireplace below the pan is laid out so as to protect the pan-bottom from the direct action of the fire and to heat it as equally as possible. The sizes of the snore-holes, etc., are all results of experience. Exactly the same sizes must be chosen if the pan is not, as drawn here, provided with a dome resting upon its own flange, but with a barrel-arch independent of it The fire on the grate *m* is covered by the arch *n*, which is pierced only sideways with holes, whose section becomes larger from front to back; thus the pan-bottom is not in direct contact with the fire. The fire plays all over the pan; but it is first kept in by the circular wall *o o*, and escapes only by its holes, different in size, according to the direction of the draught, into the outer annular space, where it heats the upper part of the pan, and ultimately into the flue *p*.

In the case represented here the pan is placed at the end of the roaster, and both are charged at the same side. Consequently the working-door of the pan is at right angles to the shoving-hole. The conveyance of the half-finished saltcake is effected by "casting" it with a long-handled shovel, curved so as to fit the pan-bottom. Such pans are called "casting-pans." If the shoving-hole is just opposite the working-door, the charge is pushed or shoved over with a long-handled rake shaped so as to fit the pan-bottom, and the pan is called a "shoving-pan." The former kind of labour is rather easier than the latter; but the arrangements must suit the locality. Sometimes placing the pan in the centre of the back of the roaster cannot be avoided, in that case the charge must always be "shoved." The fireplace of the pan may also be placed sideways, instead of endways, but preferably not at the same side as the working-door, because then the fire-cave would have to be arched over. *Sometimes the sole of the reverberatory furnace is heated from below by the waste pan-fire.*

The open roasters are heated either by coke or coal. The former is dearer than the latter, especially as the cheaper gas-coke does not answer very well, since it burns away quickly; and in the end the more expensive oven-coke pays better, because there is much less of it used Many works burn their own coke for this purpose from suitable coal. Still coke fires are mostly preferred to coal, because with the latter very much soot is formed, the fire-gas being considerably cooled by the evolution of acid vapours on the roaster-bed; and in order to prevent the pipes and condensers from being stopped up with soot, the former must be made very wide, and the latter packed very openly with loosely placed bricks. They must also be fed with a strong jet of water, in order to wash the soot off the bricks, so that it is scarcely possible to obtain strong acid. The condensed acid, mostly only 4° to 6° Tw., containing very much soot, will only do for evolving carbonic acid for the manufacture of bicarbonate, hardly even for the recovery of sulphur from alkali-waste by Mond's process (now obsolete). On the other hand, if coke is used in the roasters, the condensers can be packed much more closely, as no soot has to be dealt with; the water need not be run in a strong jet, and acid of 23° to 28° Tw. can be obtained which will do very well for making chlorine, and which, by suitable means, can be made even stronger, as we shall see below.

Muffle-furnaces (**Blind Roasters**).

The *blind roasters* (muffle-furnaces), for calcining the half-finished sulphate, are distinguished from the open roasters described above, by the fact that the flame in them does not come into immediate contact with the charge, but only acts indirectly through the bed and the arched roof, which together form a closed muffle. Accordingly the acid vapour formed in calcining is not mixed with fire-gas, and can thus be condensed much more easily than the gas from open roasters, as it is both less dilute and not so hot. It is not, to be sure, so strong as the pan-gas, as it is mixed with more air, which gets in through the working-doors during the turning-over of the charge; it is also much hotter and less pure than pan-gas, owing to the sulphuric acid escaping during the finishing operation.

At many works, accordingly, the gas from blind roasters is condensed separately from the pan-gas, especially if acid is made for sale; where all the acid is used up at the works, the gases mostly go into the same condenser. One instance of a blind roaster has already been given in connection with a lead pan (p. 94). Another construction is shown in the first edition of this work, Figs. 41 to 47, pp. 79 to 81, where the pan and the roaster have each a separate fire, which is necessary in forced work, such as is usual in England. It will suffice for our purposes here to show the section Fig. 24.

The muffle-arch behind the firebridge, where the first heat of the fire meets it, is a full brick strong, and covered besides with "half-thicks"; these are left out in the second third of the length; and the last third is only half a brick strong. The whole arch is covered with an inch of fireclay, moistened with weak soda-liquor, by which it is caused to frit together and to become more gas-tight. Of course the best firebricks must be employed, the joints must be made very narrow, and the whole masonry must be as solid as possible. The best height for the arch is 9 in.: it cannot well be made flatter without detracting from its stability; and if it is made higher, the radiant heat acts less upon the charge. It springs at a height of 12 in. from the bed, so that its crown is 21 in. above the same. The upper arch at the widest place is 12 in. apart from the muffle arch; at the narrowest (in front) it is only 6 in. Both arches are supported on metal plates covering the furnace from the outside and held together by uprights and bracing

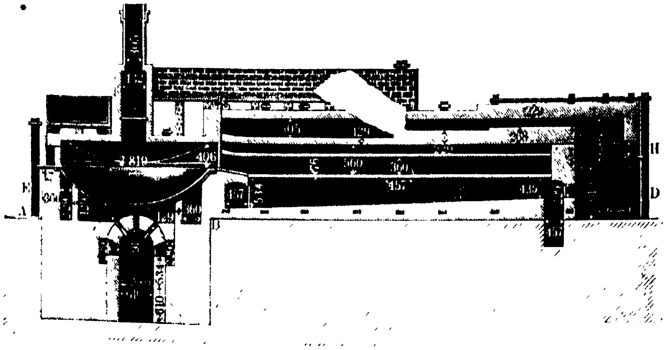

FIG. 24.

rods. In front the plates are 3 ft. high, at the back only 2 ft. They are about 1 in. thick, and on each long side require ten uprights, usually formed of 4-in. railway rails, and cross-bars of ¾-in. square- or ⅞-in. round- iron. The flames of the two fireplaces travel over the muffle-arch divided by a thin wall, and unite at the far end, and then descend by several down-draughts. Here is also the gangway between pan and roaster, together with its damper.

These parts of the furnace must be very carefully built, as they are very much exposed to wear and tear.

The gangway is all lined with metal plates. The damper has a projecting top flange for a sand lute. It wears out very quickly, and a double damper, as shown in Fig. 20 is preferable here also. Below the gangway the flues unite into a common cross flue. The flame then travels towards the front in seven narrow flues; it is here reunited by another cross flue, and at last carried towards the chimney. The seven narrow flues are so made in order to allow the furnace-bed to be made of ordinary 9-in. firebricks, which are employed on the flat, or 2½ in. thick. It is preferable to employ two courses of half-thicks (split-bricks), crossing each other. The dwarf walls separating the flues should be 9 in. thick, so as not to burn away too quickly. The flues are 5 in. wide; so that a 9-in. brick has a good hold on each side, and in the front they are continued into cleaning-out holes, usually closed. The bottom of these flues is strongly inclined towards one of the cross flues to facilitate cleaning. The acid gas is taken away by a lateral ascending channel, sometimes by a cast-iron pipe lined with bricks, passing through both arches; but the cast-iron quickly wears out, and may cause the muffle-arch to crack.

Instead of making the furnace-bed of 9-in. firebricks, at many works fireclay slabs up to 2 ft. square are employed, when the number of bottom flues is diminished to four. An nstance of this kind is the furnace represented in Figs. 25 to 27. The flame, travelling from front to back over the arch, returns in two lateral flues underneath the bed and again goes forward in two other central flues. If very good fireclay slabs can be had, the construction shown in Figs. 25 to 27 is preferable to that described above, since the bottom flues are more easily cleaned out, and there are much fewer joints in the bed. The reclay slabs must, however, be of very good quality for this, nd must be made with rabbited ends, as shown in Fig. 28.

The muffles are frequently made much longer than they are hown here—for instance, 25 or even 30 ft. long inside; they annot be made any wider, owing to the difficulty that would ccasion in turning over the charge. By making the muffle as rge as possible, the heat of the fuel is better utilised, and e layer of stuff is much thinner, and therefore much more asily turned over and mixed.

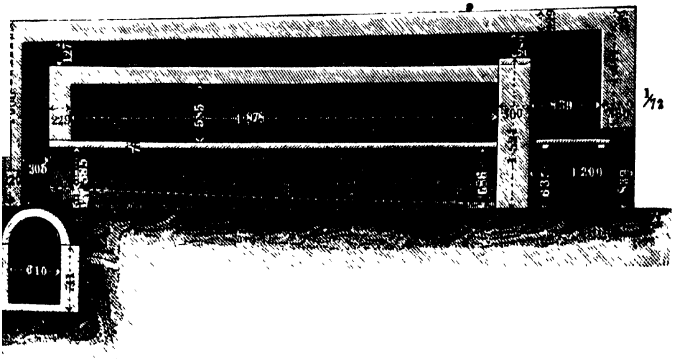

Fig. 25.

Figs. 51 to 54 and 56 to 59 of the first edition of this ook show furnaces in which the waste fire of the muffle heats he pan. We shall refer to this plan again when describing the lus-pressure furnaces.

Bair (Ger. P. 43240) constructs the ceiling of saltcake muffles y arranging a number of arches in the form of a grid, the ntermediate spaces being covered by thin porcelain slabs which ransmit the heat more easily than an ordinary brick arch. Lateral openings admit of getting at the inner thin arch for epairs without pulling down the top arch; but this must be an wkward operation after all.

[illegible] (B. P. 1098, of 1879) proposes replacing the double arch by a single arch, made of hollow bricks, the hollow spaces serving as fire-flues. (This construction must be very liable to

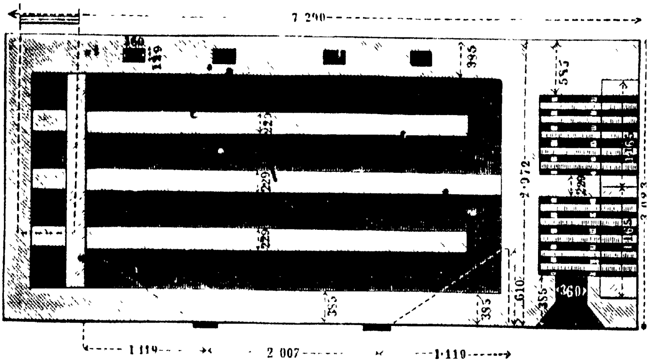

FIG. 26.

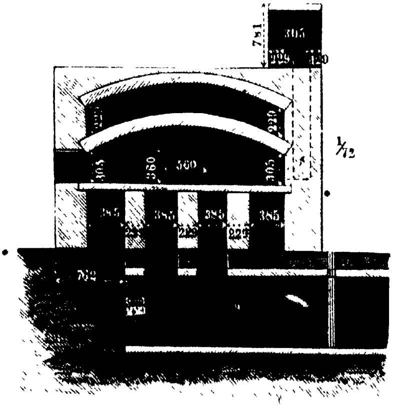

FIG. 27.

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FIG. 28.

the formation of cracks in the ceiling of the muffle, and the repairing of such cracks is very difficult.)

The plan of heating the pan by the waste fire of the muffle is not always more economical than firing the pan separately, at least not where it is considered a primary object to turn out the largest possible quantity of work; for whatever is saved in coal is more than outweighed by the increased labour, the multiplication of furnaces; etc. In the Belgian works, according to Chandelon,[1] a blind roaster decomposes about 30 to 36 cwt. of salt in twenty-four hours; in Lancashire, however, he states the daily make at 11 to 12 tons of salt. The latter is exaggerated: 5 tons of salt daily is a fair average, 8 tons a very good make for a blind roaster; 12 tons daily are only decomposed in open roasters, and even with these but rarely, 10 tons being considered very fair work. In France and Germany, even in large blind roasters, the usual quantity of salt decomposed is 2½ tons in twenty-four hours, rarely 3 tons. According to Chandelon's latest report,[2] most Belgian works then decomposed not more than 36 cwt., and very few as much as 72 cwt. With this slow work, certainly, the muriatic acid can be more completely condensed than with very quick work.

A peculiar construction is that sketched in the *Sixth Report by the Inspector on the Alkali Act*, p. 66. In order to avoid the drawback of a complicated construction, and the liability to getting out of repair, of the blind roasters, only the bottom of the roaster is fired, and that from below, thus doing away with the risk arising from cracks in the arch. The heat is very evenly distributed by flues, so that the bottom does not burn through very quickly. The flame afterwards heats the pan. Altogether the coal used is said to amount to 33 per cent. of the weight of salt decomposed. The pan-gas goes away along with the roaster-gas, which is not mixed with fire-gas. This style of furnace has not been adopted elsewhere.

Comparison of Open and Blind Roasters.

Whether *blind* or *open roasters* for calcining the half-finished saltcake are preferable, was formerly an open question. In the Tyne district none but open roasters were found, but in

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[1] *Monit. Scient.*, 1864, p. 50. [2] *Bull. Soc. Enc.*, 1871, xviii., p. 322.

Lancashire these were employed only where no strong muriatic acid was made, otherwise blind roasters alone were used. Messrs Tennant had got blind roasters at the older works near Glasgow, but open ones at the new works at Hebburn. This alone proves that something is to be said on both sides. The advantages of *blind roasters* are as follows:—

1st. Better condensation of the hydrochloric acid.
2nd. Stronger muriatic acid.
3rd. Cheaper condensing-plant.
4th. The use of coals (not coke) for firing.
5th. A saving of sulphuric acid.

The advantages of *open roasters* are:—

1st. A larger turn-out of saltcake.
2nd. Less liability to need repairs.
3rd. The impossibility of acid vapours escaping otherwise than into the condenser.
4th. Greater facility of making strong sulphate.

Of course the circumstances that appear as advantages of blind roasters correspond to drawbacks in open ones, and *vice versâ*. The defenders of each system have consequently striven to do away with the drawbacks of their system, and in many respects with success. We will now go into this matter in detail.

(1) *Condensation of Hydrochloric Acid.*—It stands to reason that the gas from the blind roasters is much more easily condensed than that from open roasters, as the latter is hot and diluted with a large quantity of fire-gas. The condensation of open-roaster gas is indeed impossible with the Woulfe's bottles, formerly general on the Continent. Owing to this, in 1856, blind roasters were made compulsory by law in Belgium. Nowadays we have got much beyond this. The bottles have been replaced partly, or even entirely, by towers filled with coke, bricks, etc., and it has been recognised that the mainspring of all good condensation is the best possible *cooling*. In modern plants the tendency is all towards the use of water-jacketed condensers, usually of glass. If a sufficient cooling- and condensing-space is provided, even the acid vapour from open roasters can be completely condensed. Indeed, whilst the former reports on the Alkali Act (up to 1867) seemed to show a much larger escape of acid vapours from open than

from blind roasters, it was discovered that the latter lost a great deal of gas through leakages directly into the chimney which could not be detected by the inspectors, since they usually, up to the last few years, merely tested for any acid vapours remaining in the gas after passing through the condensers. Since this source of loss has been more completely investigated, the reports actually showed better condensation in the Tyne district, where only open roasters were used, than in the Lancashire district. The investigations of Dr R. Angus Smith himself and of his colleagues drew the alkali-makers' attention to this source of loss, and the gratifying consequence was that much greater care was taken in the construction of blind roasters. We must take it as established that there is no proof whatever of a more *complete* condensation of the gas from blind roasters, but it is certain that the gas is more *easily* condensed than that from open roasters.

(2) *Strength of the Condensed Acid.*—In the case of blind roasters the roaster-gas is either condensed along with the pan-gas or in quite similar apparatus. If the cooling is sufficient and the supply of water properly regulated, nearly all the muriatic acid is obtained in the *strong* state, and the liquid running away from the wash-tower only shows 1° or even 0° on the hydrometer. On the other hand, the gas from open roasters is condensed in separate towers. Formerly in this way merely weak acid, only fit for bicarbonate or for sulphur-recovery, was obtained, most of which was run to waste. Latterly, however, many works, by increasing their cooling-channels, etc., have succeeded in obtaining a large portion of the open-roaster acid sufficiently strong to be employed, mixed with the pan-acid, for making chlorine. Thus the open roasters have partly made up for the start which the blind roasters had over them in this respect. It is unlikely, however, that open roasters will ever be made as efficient as blind roasters in this respect.

(3) *Cheaper Condensing-plant.*—Undoubtedly, for an equally good condensation, much less condensing-plant is used for blind than for open roasters.

(4) *Employment of Coal for Firing.*—Open roasters are mostly fired with coke, in order to avoid soot and ashes, less on account of the quality of the saltcake, if this is used up at once, than

because with coal, in spite of dust-chambers, the condensers would soon be stopped up and the disagreeable task of repacking them would occur very frequently (*cf.* p. 102). It is true that a greater absolute quantity of heat is required for a blind roaster; but although the effect of the direct flame in the open roasters is much greater, the deficiency is partly made up again by the more than double length of path travelled by the flame in a blind roaster. At all events, the fuel of the muffles is cheaper. At few works only were open roasters fired with coal, and only in cases where no strong acid was wanted, as the soot must always be washed down by means of a strong jet of water in the condensers. Nowadays this process is undoubtedly not practised anywhere.

(5) *Saving of Sulphuric Acid for decomposing the Salt.*—Such a saving is undoubtedly effected by blind roasters against open ones, as will be subsequently shown in detail.

We now turn to the points in which *open roasters seem to have an advantage*—(1) to the *larger turn-out of saltcake.* This is indisputable. The calcination in an open roaster is much quicker than in a blind one. The charge is always finished by the time the next charge in the pan is got ready, while with a blind roaster the pan-man must usually wait till the roaster-man has finished. Owing to this, a quarter or a third more saltcake is made in an open roaster than in a blind one. The pan also suffers less, as it has not to stand so many changes of temperature, which occur because the pan-man has to slacken his fire when waiting for the roaster-man. This seldom happens with open roasters, and consequently with these much more saltcake is usually got out of a pan before it cracks. The drawback in question can be avoided by putting two blind roasters to each pan; but this means a good deal more space, prime cost, and repairs.

(2) A still clearer drawback of the blind furnaces is their *liability to need repairs.* This, indeed, is their weakest point. It is against the nature of a muffle to be made of very substantial brickwork, as it would conduct the heat too slowly and incompletely. The thin hollow bottom and the arch of a muffle suffer much more from wear and tear than the solid bottom and arch of an open roaster. Besides, any considerable repair of the inner arch can only be made after removing the

upper arch, whether the latter wants repairing or not. The space between them must not be large enough for a man to work in, since, if it were, the flame would travel along the upper arch and would communicate but little heat to the lower one, that of the roaster itself. The scale turned still more against blind roasters when attention was drawn to the fact that frequently acid vapours escaped from the muffle into the outer flues, and thus got into the chimney without any condensation. Owing to this, the work had frequently to be stopped for repairs to be made, long before the brickwork had suffered very much from the heat. Later on, however, by very careful construction and by employing very good material, blind roasters were made to stand much longer and to keep much tighter; for instance, arches are made much tighter against gas by using specially moulded bricks, Fig. 29, which are joined with a very thin layer of fireclay mortar; thus the thickness of the muffle-arch can be reduced to 4½ in., and a much better heating-effect can be produced. In this respect everything depends upon the experience and skill of the manager, the mason, etc.

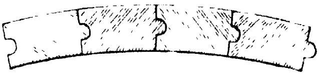

FIG. 29.

(3) *Greater Security against the Escape of Acid Vapours directly into the Chimney.*—A loss of acid-gas may take place either from the pan or the roaster. As regards the pan there is of course no difference between the two kinds of roasters, as they have the same pans, and in describing these we have seen how this fault can be avoided in constructing and setting the pans. But the roasters behave very differently. In open roasters all gas passing through the furnace, both acid-gas and fire-gas, gets into the condensers. On opening the doors and drawing the charges some acid vapour may get into the working-sheds, but this is very little; and as the workmen are the principal sufferers by it, they always do their best to avoid it. By fixing gas-hoods over the working-doors this loss may be reduced almost to zero, if the hoods are not connected with the chimney, but with a separate small condenser made of stoneware pipes,

say 2 ft. wide and 20 ft. high. In the case of ordinary blind roasters, however, there is always a stronger pull in the outer fire-flues than inside the muffle; consequently, by the slightest crack in the arch a certain, often a large, quantity of acid vapour will get into the fire-flues and escape into the chimney, without passing through the condensers. Any cracks in the furnace-bottom are less dangerous, as these, being filled up by melting saltcake, do not allow any gas to pass through; but sometimes whole tiles fall in and cause a great loss of gas. As the arch must always be thin, it is all the more liable to crack Consequently, blind roasters can never be trusted, but several times daily the air of the fire-flues must be tested by aspirating a certain volume through distilled water and titrating with nitrate of silver. It is best to test, first of all, the main flue, if there is one, into which all the saltcake-furnaces lead; if this is found faulty, the furnace-flues must be tested singly, in order to find out the individual furnaces at fault. Without this precaution large quantities of gas may escape unawares and may cause much damage and nuisance.

This very serious drawback caused some manufacturers who had worked with blind roasters to abandon them altogether for open ones; but since it has been overcome by the "plus-pressure furnaces" (see p. 113), this argument in favour of open roasters is no longer applicable.

(4) *Stronger Saltcake.*—Owing to the higher temperature of an open roaster, it is much easier to calcine the saltcake and to decompose the common salt completely. In blind furnaces this can only be attained by employing a large area and consequently a very thin layer of material, and spending a good deal of time over the calcining process. This, of course, is much easier with furnaces possessing two muffles to one pan.

Gas-furnaces.

A construction intended to combine the advantages of open roasters with those of closed ones is the *gas-furnace*, first proposed by Dr Fletcher, and carried out in practice in several modifications in Lancashire, for instance, by Mr Wigg of Runcorn. The gas produced in Siemens' generators is conveyed through an underground flue both to the calcining-furnace and to the pan. It is lighted, and the air admitted through five air-slides in the front end of the furnace. The method employed for heating the pan is a very rational one. The flame issues below its centre, and is drawn off by four flues, so that it spreads quite equally. It can be regulated at will by opening or closing the gas- and air-dampers much less than for a direct fire, and with the gas-fire the pans are much less liable to breakage. The calcining-furnace is heated by a separate gas-flue, first indirectly, through the flags forming its bottom. The flame returns over the bottom and heats the charge upon it directly. From this, however, arise several drawbacks, which have caused the system to be abandoned again in some cases In the first place, the furnace is too long, and the flame, which has already travelled underneath the bottom a distance of 30 ft., in order to return over the same, cannot bring more than a fourth or at most a third part of the furnace-bottom to a heat sufficient for finishing the sulphate. This can be avoided by making two beds of 15 ft. length each, assigning one of them to each pan. But even then the sulphate easily fluxes through the joints of the plates and stops up the flues underneath. This happens much more readily than with ordinary blind roasters, because here the flame travels first over the arch and then under the bottom, which thus does not get so hot. The object of the arrangement was to produce, by means of the gaseous fuel and the regulation of the air, a flame quite free from smoke and not containing a large excess of air, and thus permit the production of as much strong muriatic acid by a reverberatory furnace and a coal fire as with a blind roaster; but this has not proved to be the case. Moreover, this, like all other gas-furnaces for decomposing salt, consumes more fuel than hand-fired furnaces, no doubt because in this case the principle of recuperation of the heat has not been, and perhaps cannot be, sufficiently observed.

Gamble's gas-furnace will be described below, as it belongs to the plus-pressure furnaces.

Plus-pressure Furnaces.

This name has been adopted for a type of furnace introduced in 1876, in which the escape of acid-gas through any leaks in the muffle into the fire-flues, whence it goes directly into the air, without passing through the condensing apparatus, is avoided as follows: The draught within the muffle is made stronger than in the fire-flues surrounding it, which means a "plus-pressure" in the latter. In the case of any leaks in the muffle the acid-gas will not escape from this into the flue, but on the contrary a little fire-gas will enter the muffle. This does comparatively little harm, and at all events stops the formerly ceaseless complaints about the escape of hydrochloric acid from the chimneys.

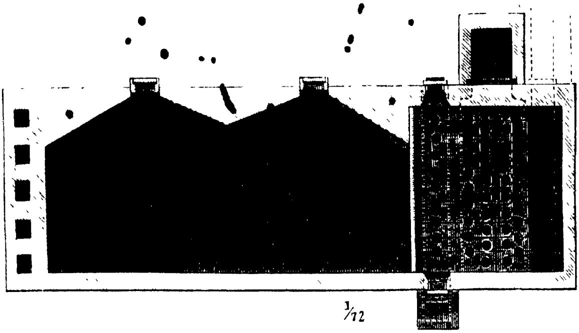

FIG. 30.

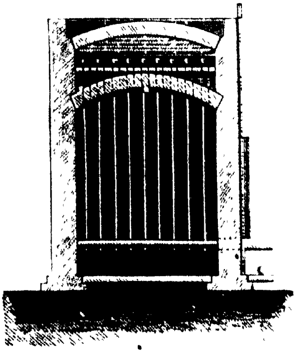

FIG. 31.

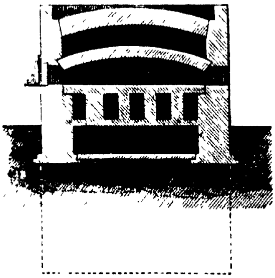

FIG. 32.

The object in question can be attained in various ways.

Muspratt (B. P., 4th May 1877) causes an excess of pressure in the fire-flues by dispensing with chimney-draught and forcing air underneath the grate instead. He also admits more air in other parts of the furnace for burning the carbon monoxide. Gamble's furnace is represented in Figs. 30 to 33. Here a blind roaster is fired by means of gas-producers; the air required for combustion is heated by passing through a system of iron pipes, which, on their part, are heated from the outside by the waste heat of the furnace-fire. The escape of acid vapours from the muffle into the fire-flues, through any chinks, is to be avoided by carefully adjusting the dampers so as to put the gas in the generator under a somewhat higher pressure than the gas inside the muffle. This is not very easy, since the pressure inside the muffle varies considerably, according to the rate at which acid vapours are given off; but with a little care the object can be attained. In another furnace, built later on at the same works, the ash-pit was closed and the air necessary for combustion was forced in by a Roots' blower partly below the grate, partly after being heated in the above-mentioned iron tubes, above the fire, in order to complete the combustion.

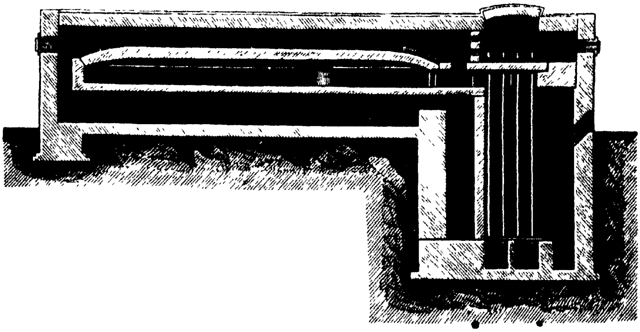

FIG. 33.

Identical in principle with this are other constructions, in which the blast of air is produced by a fan-blast or by a steam-injector. The last-mentioned process has been found least economical, as might have been predicted.

In a very good Gamble's furnace, the principal portion of the air was superheated to 650° by a large number of iron tubes 9 ft. long. It then entered the furnace through four pipes just over the fire-bridge, passed first over the muffle-arch, then underneath its sole, and brought the muffle to a bright red heat right up to the back end. Here twenty charges of 16 cwt. of saltcake were made every twenty-four hours, or 100 tons in six days. The cost of fuel was 2s. per ton of saltcake, inclusive of the (specially fired) pan, which meant a saving of 33 per cent. against the previous state.

Deacon's Furnace—The plus-pressure furnace most widely employed, and which may be considered the best, is Deacon's; it is certainly very simple in construction and working. It is shown in Figs. 34 to 37, on a scale of $\frac{1}{96}$. Its principle is simply this:—The fire-grate is placed at a considerable depth, about 11 ft., below the top of the fire-bridge, whereby a chimney-like shaft, *a* (3 ft. 6 in. × 4 ft. wide), is formed, in which the gas rises from below the bars with a good deal of pull, so that further on, that is round the muffle, all the less draught is required. To aid in this, Deacon at first arranged "breaks," that is, holes in the flue leading from the furnace to the chimney, through which air was allowed to enter, in order to diminish the pull round the muffle; but this was abandoned later on. In the shaft *a* there are two air-holes, serving also for cleaning out ashes, below the fire-bars, which are 2 ft. 6 in. above the bottom of the ash-pit. The bottom of the fire-door is 19 in. above the bars; the fire-door itself is 10 in wide and 15 in. high; above it, just below the fire-bridge, there are again two holes (8 in. × 12 in.) for introducing air. Everything else can be seen quite well from the drawings. In these the pan is protected against too strong an action of the fire by making the flues below it very deep. In other cases, where it was awkward to go too much down into the ground, shallower flues have been made and the pan has been protected by a curtain-arch. The fire-gases issuing at E are best carried underneath a pan for warming up the acid, before going into the main flue.

The introduction of the plus-pressure furnaces has not merely put an end to the complaints about leaking arches, which led to frequent stoppages for repairs, but has also produced everywhere a considerable saving of fuel, about 30 per cent ; probably because it was necessary to regulate the supply of air both below and above the fire-grate with great

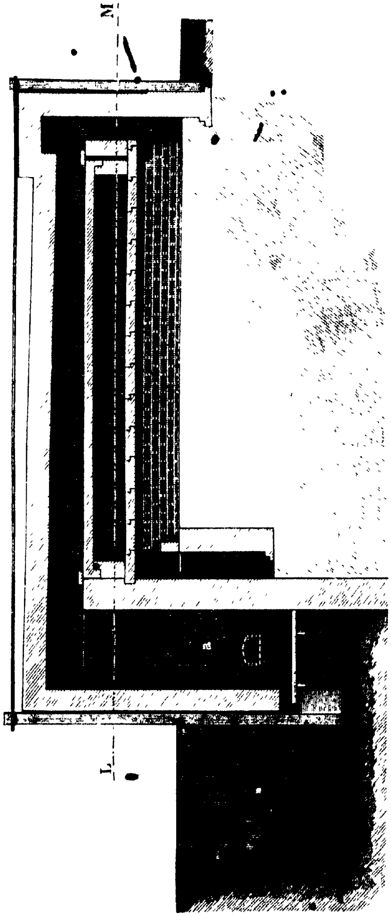

FIG. 34.

nicety, which led to more careful firing altogether. From figures given by Gamble in the *Seventeenth Report on the Alkali Acts*, p. 44, it is clearly seen that formerly much too little air

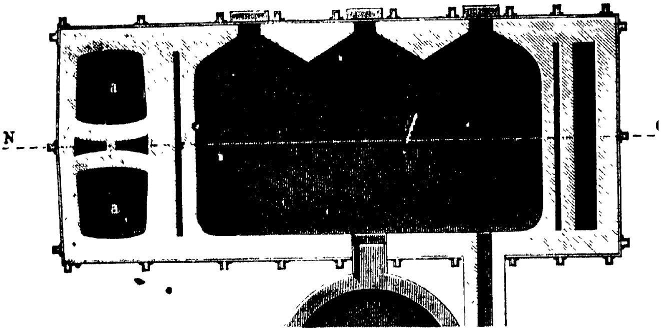

FIG. 35.

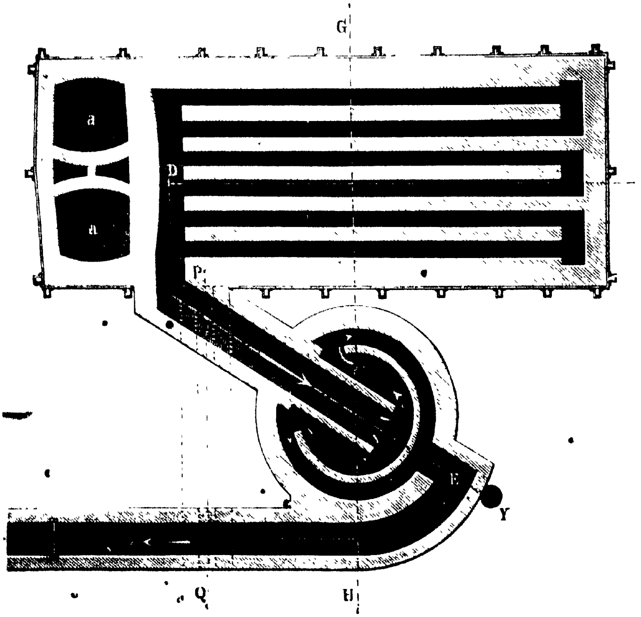

FIG. 36.

was used in the combustion, and much carbon monoxide was formed. This drawback was done away with by admitting heated air above the fire-grate, and the fire-gases now averaged

16·3 per cent. CO_2 and 2·4 per cent. O, with mere traces of CO. The consumption of fuel, which was formerly from 7½ to 10 cwt., went down to 4½ cwt.

According to the *Alkali Report for* 1891 (No. 28), the plus-pressure furnaces were constantly gaining ground over the mechanical furnaces, because they produced more strong hydrochloric acid; but the *Thirty-eighth Report* (for 1901) states that coal suitable for plus-pressure furnaces cannot be obtained everywhere.

Recently the use of mechanical furnaces has been extending, and the present tendency appears to adopt them.

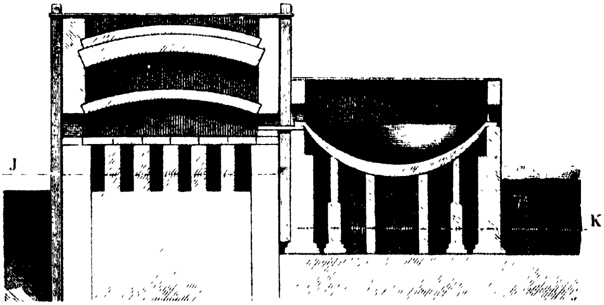

FIG. 37.

One drawback connected with the plus-pressure furnaces is not mentioned in the publications thereon, but is caused by the nature of things, namely, the greater dilution of the gas in the muffle as compared with ordinary blind roasters. According to trustworthy communications from a competent source, the gas from plus-pressure furnaces contains only from 100 to 200 grains HCl per cubic foot, equal to from 12·3 to 21 per cent. by volume, together with some steam and a little SO_2 and SO_3. In England it is not easy to make from it stronger acid than 30° Tw. On the Continent, where troughs and stoneware bottles in front of the coke-towers are more abundantly employed, the acid can be made stronger than the above.

Saltcake-furnaces worked with High-pressure Gas.—Zahn[1] states that these are quite different from the ordinary plus-pressure furnaces, in which there is a great excess of air which, as he says, acts injuriously as to wear and tear. When real high-pressure firing is employed, that is, gas-producers with a very deep layer of fuel, the utilisation of the heat is much better and the wear and tear less, since the flame is purer. [This distinction looks decidedly artificial. Furnaces worked by producer-gas are only a kind of plus-pressure furnaces, already well known. To this class belong all saltcake-furnaces in which the gases do not have a tendency to escape from the muffle into the fire-flues, but *vice-versâ*.]

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[1] *Chem. Zeit.*, 1905, p. 623.

Reuss[1] states that the high-pressure gas saltcake furnaces are more and more spreading in Germany.

General Rules for Saltcake-furnaces.

The following rules hold good for all saltcake-furnaces. It is advisable to paint, not merely all the metal parts, but the whole of the brickwork outside, with hot coal-tar, and to repeat the painting when the furnaces are hot. Thus both the iron and the brickwork will be protected against the rapid corrosion to which they would both be subjected by the muriatic acid vapour Thus protected, an open furnace goes a long time without any important repairs, except occasionally renewing the lining of the fireplace. But, in the nature of things, the muffle of a blind furnace cannot but require frequent repairs. In the first place, it must be very thin, so as to be more readily penetrated by the heat, secondly, its outside is acted upon by the fire and its inside by the acids, and the bottom is injured by the mechanical labour of turning over the saltcake; thirdly, even the smallest crack must not be neglected, but the furnace must be stopped in order to repair it, so as to avoid losses of acid vapour. Consequently, it is much better not to place the acid-gas flues on the top of the arch, but sideways.

In regard to the brickwork of the pan, the lining of the fireplace and the arch over the grate suffer rather much if the work is pushed hard, and must be pretty frequently renewed. The upper part (or, in case of heating by waste heat, the whole) of the fire-flues suffer very little. The arch over the pan, if built independently of it and well constructed, may last out several pans.

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[1] *Chem. Zeit.*, 1908, p. 231.

Process in Saltcake-furnaces worked by Hand.

The process with cast-iron decomposing-pans is distinguished from that which is carried on in lead pans principally in that it can be accomplished much more quickly, because greater heat can be employed and there is no fear of the tools injuring the pan. Working for a large turn-out is consequently possible with cast-iron, but not with lead pans.

The pans, after moving their contents into the roaster, must be cleaned from crusts as much as possible; to purposely leave them in the pan, as is described in some places, is a grave mistake; for in the unavoidable interval up to the introduction of the new batch such crusts burn fast, and cannot be dissolved again, causing the pan to crack before its time. Nearly all cracks in pans can be traced to the formation of crusts through unskilful or negligent work, except such as are owing to faults in casting, to bad setting, or to fair wear and tear; the former will come out almost immediately after starting a new pan, the latter only after a long time. After removing the crusts the pan is allowed to cool down a little, by opening the fire-door or by shutting off the gas in the case of gaseous fuel; in any case the pan must cease to be red hot, else it will suffer from the cold, damp salt, and even more from the vitriol; at the best the evolution of hydrochloric acid will in this case be much too violent and cause the pan to boil over, blowing off gas through all the joints, and rendering the condensation incomplete. In small works it may be possible to do as some advise—to dry and heat the salt before charging. In large works this would be too troublesome, and the salt is nearly always put into the pan direct from the warehouse, with its natural moisture, usually varying from 2 to 7 per cent. according to circumstances. It is mostly shovelled in at the working-doors. Hoppers for charging from the top are not frequently used, both because they much increase the weight upon the arch, and because the pan-men have at any rate time for charging. Besides, the pan-bottom is cooled too quickly if the whole mass of salt is suddenly let down into it, and in this case at least, the vitriol ought to be heated pretty strongly and run into the pan *first*. It will not do to rely upon the salt sufficiently drying and heating within the hopper in the interval before the next operation. Usually there is a metal plate in front of the working-door, and the quantity of salt weighed off for each charge has previously been laid down upon this plate against the pan-furnace, so that nothing is left to do but to shovel it in.

The quantity of salt taken for each batch varies very much in different works. Batches below 5 cwt. of salt are as rare as those above 10 cwt for open roasters, or 16 cwt. for close roasters (in the latter case taking twice as much time). The usual quantity in English works is 8 or 9 cwt. for open roasters, 14 to 15 cwt. for close roasters Charges up to 1 ton are, however, not unusual. On the Continent, where close roasters are all but universal, mostly smaller batches are made—for instance, at Aussig twelve batches of 8 cwt. each in twenty-four hours, at Stolberg eight batches of 6 cwt. each in twenty-four hours.

The purity and concentration of the *sulphuric acid* have already been considered (see p. 56), and its measuring, heating, and running-in (see p 95). As to the temperature of the vitriol, manufacturers are not agreed. It ought never to be below 50° C.; but some use it upwards of 100° C. For the pan, the hotter the sulphuric acid the better; but if it is too hot, the hydrochloric acid is given off too fast, with the consequences previously described; there is always, therefore, a medium to be observed. The temperature ought to be always approximately the same, in order to regulate the *quantity* of the vitriol—which is always measured, and whose volume is considerably altered by great changes of temperature. Temperature corrections would make the measuring very complicated, when added to the unavoidable corrections for differences in the strength of the sulphuric acid and the degree of moisture of the salt. Usually the moisture is tested once a day in the laboratory, and special tables enable the workmen to reduce the quantity indicated to them to that corresponding to the strength of acid they may happen to receive from the chambers.[1]

The theoretical ratio of pure sulphuric acid to pure sodium chloride is 49·04 to 58·46, or 83·83 parts sulphuric acid to 100 parts sodium chloride. As acid of 144° Tw., measured at 15° C., contains 78 per cent. H_2SO_4, 100 parts of pure NaCl answer to 107·44 parts of vitriol of 144° Tw. Now pure NaCl is never employed; for instance, for a 95-per-cent. salt the requisite quantity of acid would be 79·62 per cent. of H_2SO_4, or 102·07 per cent. of acid of 144° Tw. In practice, somewhat more acid must be employed, especially if saltcake for alkali-works has to be made; but other cases may occur as well. If, for instance, the saltcake is to be as strong as possible, more than the theoretical quantity of vitriol must be taken; for, as it is impossible, at least in hand-worked furnaces, to mix all parts uniformly and instantaneously, a little sulphuric acid will be volatilised in some parts of the mixture, where it is in excess, whilst undecomposed common salt remains in other parts. If, therefore, the percentage of salt in the finished product is to be 1 per cent. or below, a little more vitriol must be employed, say 1 or 1½ per cent. calculated as SO_3, in addition to that volatilised with the hydrochloric acid vapour.

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[1] Such tables are given in Lunge's *Technical Chemists' Handbook*, pp. 126 to 129.

Some of the largest manufacturers assume, in the calculation of the sulphuric acid produced at their works, which is not measured directly, that for each 100 parts of salt of average moisture, say 5 per cent., 81·33 parts of H_2SO_4 are employed for making strong sulphate in open roasters. In this case Lunge found 82 per cent. necessary, and obtained from other factories the figures 82·5 per cent. for open, and 79·3 or 80·8 per cent. for close roasters.

If, on the other hand, the saltcake is required to be entirely *free from acid*, for this very reason rather less than the theoretical quantity of vitriol must be employed, so that 2 or 3 per cent. NaCl remains in the finished product. This should not be done for making alkali.

In any case a larger excess of vitriol is used in open than in close roasters—in the former often 5 to 7 per cent. above the theoretical quantity, because the greater heat and the direct draught carry away a portion of it before it has had time to act upon the salt, whilst the excess required for the slower work in blind roasters amounts only to 2 or 3 per cent. The statement of Wright[1] is, however, exaggerated, according to which the average loss of vitriol in open roasters would be 12·6 per cent., that in blind roasters 2 per cent.; the former figure is not derived from his own experience, but from second-hand information; and it is in decided contradiction to the experience of the

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[1] *Chem. News*, 18, 17.

Tyneside factories, all of them working with open roasters. We shall have to revert to this matter at the close of this chapter.

In mechanical furnaces a little less sulphuric acid is used than even in blind roasters, just because the mass is much better mixed up, and especially because it is always in the state of fine powder, without any lumps and knots. It is in the interior of the lumps there is most facility for incompleteness of decomposition; consequently those furnaces turn out sulphate containing only a small fraction of both free acid and common salt.

In the ordinary process such lumps are formed in the pan only with very faulty work; for, under normal conditions, the whole is at first dissolved into a thin mud, which only gradually thickens, but never solidifies. On the other hand, lumps are very readily formed in the roaster.

The proper quantity of sulphuric acid cannot easily be determined beforehand by mere calculations, owing to the complication of circumstances coming into play; it must therefore be continually checked by testing the saltcake in the laboratory. We have spoken of this already on p. 122.

In most factories the residue from decomposing the nitrate of soda, the *nitre-cake*, is put into the pans along with the salt, the quantity of sulphuric acid being lessened by the amount of that existing in the nitre cake as "free acid"—that is, as bisulphate. It is preferable for regular work not to use too much nitre-cake, say one-tenth, or better only one-twentieth of the salt; otherwise lumpy, poor sulphate is frequently obtained. Nitre-cake is often used in large lumps; but it is much better to grind it, in which case more can be taken and the quality of the finished product will be less injuriously affected. Possibly the best way of treating it is to run it into the pan in the liquid state, as will be described later on.

The requisite quantity of sulphuric acid is frequently run into the pan before the whole of the salt has been shovelled in, by which a better mixture is effected. In any case, it must be well stirred up afterwards with a long-handled rake, till the acid has completely penetrated into the salt and a thin mud has been formed in which the tool does not meet with any resistance; this is called "dissolving the salt." As a very strong evolution of gas takes place at this stage, it is well if the working-door has a hole through which the handle of the rake passes; by heaping a little salt against the opening, a pretty tight closing is effected. At this stage the mass has a strong tendency to rise and froth over; consequently a little tallow is now added. The porous common pan-salt dissolves by far the most easily, much less so ground rock-salt, as mentioned on p. 55. When everything has been "dissolved," the rake is drawn back so that its blade lies close against the door, where it is less exposed to the acid; or it is drawn out altogether after opening the door. In any case the latter is now closed as tightly as possible, either by salt thrown against it, or even by plastering it with clay or lime. Well fitting cast-iron doors, sliding in frames, make this unnecessary, but do not resist the effect of the acid vapours very long. The door-frames are consequently mostly made of acid-resisting stone or of stoneware, as is also the frame of the damper separating the pan from the furnace. The door itself is made of lead, slate, or even of cast-iron, but iron lasts only a short time. At some German factories wooden doors are preferred. Most usually the doors are only loosely placed against the frame, and luted by salt belonging to the next charge.

Vapour-hoods.—In most cases, during or shortly after raking up the fresh batch, when the evolution of gas is most vehement, but especially on shoving the batch from the pan into the furnace, the escape of a little hydrochloric-acid gas into the outer air cannot be prevented. If the condensing-apparatus works properly, it cannot have a great draught, and with the working-door standing open this draught frequently will not suffice for removing all the gas. This also holds good for the working-doors of the roasters, especially on discharging, and even for the damper between the pan and the roaster. In order to avoid a nuisance for the workmen and the neighbourhood, it is advisable to fix over the doors and the damper *vapour-hoods*, made of wood or light cast-iron, etc., which communicate by means of fireclay pipes with a well-drawing chimney. The quantity of acid vapour escaping into these is mostly so inconsiderable that, after being diluted with the chimney-gas, it is not perceptible. If, however, this source of escape must be avoided at all costs, the fireclay pipes may be conducted into a small special condenser, but this will certainly only furnish an extremely weak and practically worthless acid.

Works with very large condensing-space can employ sufficient draught to dispense entirely with hoods.

The ordinary vapour-hoods, when they are connected with an ordinary chimney, usually do not suffice for keeping all vapours out of the working-space. There is also a nuisance caused by the condensation of acid drops at their bottom edge. These drawbacks are avoided by an arrangement of K. Oehler (Ger. P. 165099, of 1904). He provides in the roof of the working-hole a slot, which can be closed by a damper, and through which a strong suction is exercised during the time the door is open. The muffle-bottom is also provided in front of each door with a slot, which can be hermetically closed, and which is connected with a flue, carried along underneath the doors and ultimately outside the furnace, into a closed iron box. In this flue there is a mechanical conveyer which carries the saltcake, pushed into the slots after finishing the operation, into the iron box, where it cools down without contact with the air. The acid vapours, sent out by the hot saltcake during this time, are driven by means of a stoneware fan ("Siegfried" system) into a side-condenser, consisting of a tower, 3 or 4 ft. wide and 12 to 15 ft. high, with a water spray on the top This converts all the acid into a fog; when this settles at the bottom and runs out, it appears as dilute hydrochloric acid, containing much H_2SO_4. This is employed for running through the back tower of an ordinary condensing-plant. Behind the small condenser is placed the stoneware fan, and ultimately a gas-filter, as described in a following chapter. An analysis of the tower acid showed, as the average of four days, 4·8 per cent. HCl, 0·24 per cent. H_2SO_4, 0·007 per cent. Fe_2O_3; sp gr. 5·4° Tw., when employing in the tower 40 per cent. of the total water required for condensing the HCl in the process. (This plan was at work for some time, but seems to have been discontinued again.)

When the "dissolving" is finished, the mass need only be stirred up once every quarter of an hour, but the fire must be increased exactly as required for concentrating the mass. Generally the operation in the pan is finished much sooner than that in the roaster; but the roaster charge must by all means be finished and drawn out of the furnace before the batch is finished in the pan, for otherwise the latter becomes too stiff, cakes to the pan, and cannot be manipulated at all. The fire must be regulated to accomplish this, and also in such a way that the boiling does not become too violent. On the other hand, the pan should not work so slowly that the furnace must wait for it and stand still in the meantime; but this will hardly ever happen if the sulphuric acid be above 124° Tw. The whole operation in the pan lasts, in the case of open roasters, one hour, with close roasters from two to two and a half hours, on the Continent even longer, according to the time the batch stops in the roaster.

A different style of working was introduced by the Newcastle Chemical Works at Gateshead. Large pans are used, 18 cwt. of salt being treated in them at a time. Every hour one-half of the batch is shoved into the (open) roaster, and another 9 cwt. of salt, together with the corresponding quantity of sulphuric acid, is put into the pan. In this way the pan never becomes empty, except at the end of the week, and suffers much less than usual, so that up to 4000 tons of sulphate can be got out of it before it becomes useless. The work is done in the following way:—On beginning the week, 18 cwt. of salt and acid to correspond are introduced into the pan; when the mass has thickened up to the usual point, half of it (by the judgment of the eye) is shoved over into the furnace; then the sulphuric acid requisite for another 9 cwt. of salt is run in, the mass raked through, 4½ cwt. of salt added, raked through again; the fire is touched up, the last 4½ cwt. of salt are added, raked through, and the batch finished in the usual manner: when it has become stiff, half of it is again shoved into the furnace, and so forth. This style of work has been very successful, and has been introduced by several other large factories.

The batch in the pan is considered finished when the cake cannot be drawn backwards and forwards with ease, but offers considerable resistance owing to the stiffness of the mass. If the setting of the pan is faulty, lumps cake on the hot places of the pan, and are only dispersed with difficulty or not at all. Supposing the contents of the pan to have become stiff, and the roaster-bed to have become empty in the meantime, the damper is raised, the pan-door opened, and the stirring-up rake (Fig. 38 *c*) replaced by the tool that serves for moving the batch. For pan-doors opposite to each other (shoving-pans) this is a "shoving-rake," Fig. 38 *d*, the profile of which is the same as that of the pan; for pans with doors at right angles to each other (casting-pans) a large hollow "casting-shovel," Fig. 38 *e*; and whilst the pan-man moves the contents of the pan into the furnace, the furnace-man from his door at once spreads the charge evenly over the whole furnace-bed.

The *calcining-furnace*, before the charge is moved, should be at a bright-red heat, as it will be after finishing the previous charge. With blind roasters, at least, the arch should always remain red hot, so that the interior can be seen. The fresh batch, of course, greatly cools the furnace, and its interior becomes even less visible in consequence of the thick white acid vapours given off. Towards the end of the operation the temperature should get up to a good red heat, but always below the melting-point of sodium sulphate (which is 860 to 880° C.), say, about 800° C. The mass is spread over the furnace-bed with great care—if the furnace is a double-bedded one, on the top (back) bed; there it is first allowed to dry and is turned over every quarter of an hour, employing partly the paddle or slice, Fig. 38 *a*, partly the tooth-rake, Fig. 38 *b*. In Lancashire the latter tool is less used than the former; but it contributes very much to an even working-up of the mass, as it prevents the formation of lumps. All the tools are made entirely of wrought-iron, the

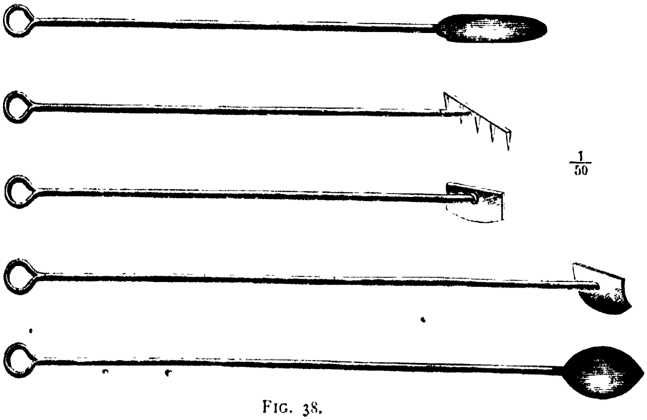

FIG. 38.

handles ⅞ or 1 in. thick and 12 to 15 ft. long. The working-parts of the paddles, rakes, etc., being also made of wrought-iron, are much lighter than those of the black-ash furnaces, whose heat is much greater, but they are quickly spoilt by the acids and must be frequently renewed.

In order to take part of the weight of the tools off the men, there are always fixed in front of the working-doors horizontal bars, with a few projections on the top; and hooks hang down from the ceiling, for supporting the back part of the tools.

When once lumps have been formed, they can only be broken or crushed with the paddle. This ought to be done in any case. If, however, the batch has become too hot next to the fire-bridge, it fluxes there and the tools cannot be got underneath it. This is the worst thing which can happen, because such hard lumps are scarcely workable in the black-ash furnace; it occurs especially with inexperienced men, and can only be avoided by frequently moving away the stuff next to the fire-bridge and replacing it by other stuff. Weak saltcake, containing much salt, fluxes much more readily than strong saltcake.

There is less trouble in this respect with open roasters, because the workman can always see what he is doing. Their beds, for an equal make, need only be half as large as those of blind roasters. Often open furnaces have two or even three beds, sometimes arranged in terraces, or merely marked by the greater length of the furnace and the arrangement of the working-doors. In this case the batch coming from the pan is first spread on the back or top bed, and moved forwards to the front bed, which is much hotter, when the previous batch has been drawn out from the latter. Thus the saltcake remains twice or three times as long in the furnace as in single-bedded furnaces, and can be finished at greater leisure. If, for instance, a batch is made in the pan once an hour, this batch remains one hour on the cooler back bed and another hour on the hotter front bed before it is drawn out. In blind roasters the batch is usually at once spread evenly over the whole bed, because here the differences of temperature are not very considerable.

The calcining work is only to be taken as finished when no more vapours are given off by the mass, even on turning over, and when it is at a red heat; but it ought not to attain the fluxing-point at any place. The mass is now drawn out by means of rakes, Fig. 38 *c*, into iron barrows, adapted for tipping over. Fig. 39 shows such a barrow of the shape usual in England. They suffer a good deal from the acid reaction of the saltcake; and their upper portion must be frequently renewed. At large works there is often a railway running along the furnaces, and four-wheeled trucks run upon this up to the furnace-doors. In front of these there is always a metal plate, because some saltcake (which must be kept clean) is always spilt. The front of the furnace below the door must be protected in a similar manner.

In many cases the finished saltcake is not drawn directly into the barrow, because in this operation the escape of acid vapours could not be avoided (which in populous districts might be felt as a nuisance), but it is dropped into a *cave* below or in front of the furnace, by means of a hole in the furnace-lid usually kept closed; here it can cool down before it is taken out. Fig. 40 shows such a cave in section at A, as well as the hole *a* in the furnace-bottom leading to it; Fig. 41 shows it closed with its door, *b*. This arrangement was very rarely found in English works; with the hard-pushed style of work in use in this country it could scarcely be carried out, not merely because it requires much labour to move the saltcake twice instead of once, but especially because the taking-out of the saltcake from the cave would interfere with the furnace-work, and there were not, as is usual on the Continent, long intervals between the charges which might be utilised for emptying the cave.

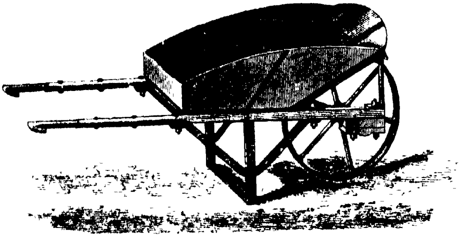

FIG. 39.

It is just this part of their operations which rendered the English alkali-makers the objects of many complaints from their neighbours, if their saltcake furnaces and warehouses were not at a good distance from public roads, fields, etc. Such complaints were met to some extent if care was taken at once to cover the hot saltcake in the barrows and the storehouse, which, especially in damp weather, emit much vapour, with a thin layer of cold saltcake.

These pungent vapours, inevitably given off during this operation, which greatly distress the workmen even when they are prevented from being a nuisance to the neighbourhood, are entirely prevented by allowing a fine spray of water to play upon the hot saltcake, at a distance of about 3 ft., from a jet exactly like those very advantageously used in the vitriol-chambers. This fine spray condenses the vapours to such an extent that no smell is perceptible close by, and does not cause the hot saltcake to become damp. There is an evolution of steam, but no "gas." This simple contrivance deserves serious attention with a view to preventing nuisance. In some cases, brine has been used instead of water for spraying the hot saltcake. This is highly objectionable as it leads to the evolution of more hydrochloric acid whenever the saltcake is even slightly acid.

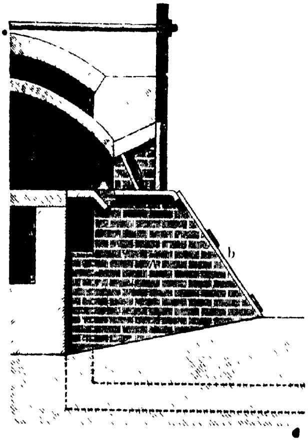

FIG. 40.

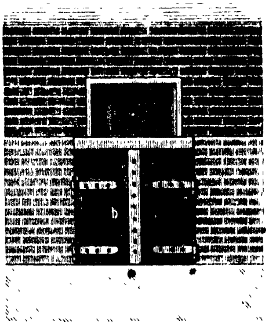

FIG. 41.

Sometimes, instead of caves, iron boxes mounted on wheels are employed for drawing the saltcake. In other places the caves are placed underneath the furnaces and are large enough to hold a whole day's make. Fig. 42 shows this arrangement. Behind the furnace-doors cast-iron pipes, 12 in. diameter, are carried in a slanting direction downwards through the arch of the cave. The latter is connected by means of other pipes with the hydrochloric acid condensers, preferably with a special small condenser, which is connected with the chimney. The bottom of the cave is formed by a cast-iron plate, below which

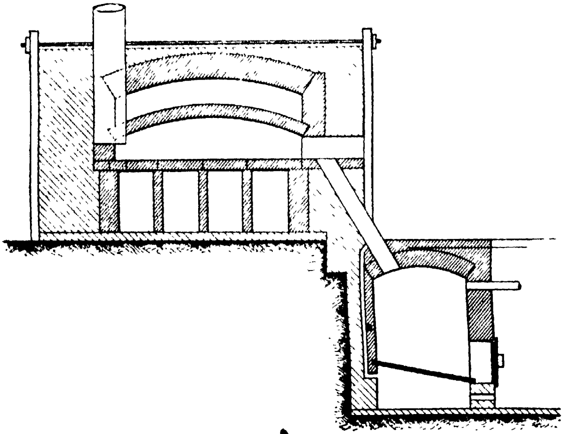

FIG. 42.

cold air is introduced by means of holes in the wall. This air rises upwards in slots in the back-wall of the caves, and thus cools that wall as well. The saltcake is not taken out of the cave before it has sufficiently cooled down, and as long as it continues to give out vapours, which generally takes about twelve hours. Then only is it removed by means of a lift.

The vapour given off by fresh hot saltcake consists mostly of sulphuric acid or anhydride, if the operation has been so conducted as to furnish a strong saltcake, but of hydrochloric acid in the case of weak saltcake (with 3 per cent. NaCl or more). The prickling smell of the latter acid on drawing the batch permits a kind of judgment to be given upon the strength of the saltcake.

Whether the work in the furnace has been good, is judged partly by the appearance of the saltcake, partly by testing. The properties which good saltcake ought to possess have been described on p. 60; it should be a finely grained, yellowish-white mass free from lumps. The red colour often exhibited by the lumps does not prove that they contain more iron than the remainder, but merely that the iron, contained in the white saltcake as nearly colourless sulphate, has passed over into red ferric oxide at the higher temperature, which has caused the lumps to be formed.

The lemon-colour shown by hot saltcake, even such as becomes quite white on cooling, seems to come from iron; for it is not shown by the saltcake made in the mechanical furnaces, which contains less iron.

For any irregularities in the outward appearance of the saltcake, such as lumps, fluxings, unequal calcination, etc., the furnace-man (roaster-man) will have to be made responsible—also if the analysis shows that much free acid is present together with much undecomposed salt. But if a fair average sample shows only either too much salt or too much acid, this is the fault of the pan-man, and the mixture has then to be changed. Saltcake not containing above ½ per cent. free NaCl and 1 per cent. free acid (calculated as SO_3) was formerly called very good, but nowadays even greater purity is called for, as we shall see when speaking of yields.

Special Methods of making Saltcake.—Wigg (B. P. 5105, of 1879) proposed keeping out the air more than is otherwise done when working saltcake furnaces, in order to get stronger acid. This was to be done by passing superheated steam into the furnace. It is doubtful whether the cost and other drawbacks of this process do not outweigh its advantage. It is true that it is useful to saturate the gases with steam, as we shall see in Chapter VII., but this can be done more cheaply by the heat of the gases themselves.

Pedder (B. P. 4712, of 1891) proposes a very peculiar style of work. Rock-salt is to be mixed in a Weldon still with a sufficient quantity of sulphuric acid, to which a third of its bulk of hydrochloric acid has been added, and the decomposition is to be promoted by steam. The liquor is to be run off for crystallisation, and the mother-liquor [which is greatly diluted !] *is used over again* in the next treatment of salt. The crystals are roasted [what does this mean?], in order to drive out the hydrochloric acid. The vapours, as well as those from the still are passed into a condenser. In lieu of a Weldon still, the work can be done in ordinary saltcake furnaces, in which rock-salt is treated with a mixture of sulphuric and hydrochloric acids at such low temperature that no bisulphate is formed. [This passage is quite absurd, and the idea of making rock-salt more easily decomposable by adding hydrochloric acid to it is also very crude.]

Walker (B. P. 22853, of 1854) mixes with common salt sufficient sulphuric acid to form an acid sulphate, which is treated in one of the following ways:—Either it is cooled, roughly ground, mixed with monosulphate and salt, and heated in a second furnace with a mechanical stirrer; or else it is run out of the first furnace in the fused state over a weir into another compartment, where the mixing takes place. To obtain nitric acid, nitrate of soda is treated in the same manner. [Neither of these processes has any economic value.]

Th. Meyer, in his Ger P. 186398, proposes a style of work entirely different from the ordinary method. The common salt is dissolved in a great excess of hot bisulphate, which is easily done in a cast-iron pot. At the same time concentrated sulphuric acid, with at least 90 per cent. H_2SO_4, is run in. In consequence of the difference of the specific gravities of fluxed sulphate and sulphuric acid, a regular circulation of the latter and good mixing goes on without manual labour, and dry, highly concentrated HCl is given off. The fluxed bisulphate is contained in a semi-globular pot which is heated externally. Into this is fed continuously ground salt and 93 per cent. sulphuric acid, while at the bottom the resulting mixture of salt and partially decomposed bisulphate is constantly run off. (This process hardly applies to a regular manufacture of saltcake, but to that of highly concentrated hydrogen chloride and of bisulphate, which must be utilised in some other way.)

Mechanical Saltcake-furnaces.

Up to the year 1875, the process of decomposing salt was universally conducted by one or other of the methods described above, but the mechanical furnaces came so rapidly into favour that they for a time threatened to oust the hand-worked furnaces. The disadvantage that they gave a weaker hydrochloric acid proved serious, and by 1900 the tendency was to revert to the older form. Since then, however, mechanical furnaces have been improved in detail and their use is at the present time extending. There are two serious drawbacks to working with hand-worked furnaces which cause it to be a very disagreeable business. The first of these is the sometimes unavoidable escape of pungent hydrochloric-acid vapours, issuing on stirring up the charge in the pan and roaster from the working-doors, which are, of course, very troublesome for the men and are also injurious to health, although not to the same extent as chlorine or nitric-acid vapour, so that the saltcake men on the whole are not the worst off in that respect among chemical workmen, of which they form one of the best-paid classes. But in bad weather, and with insufficient draught, sometimes thick clouds of acid vapours issue from the decomposing-shed and cause a nuisance in the neighbourhood. It will not do to stop this by increasing the draught in the condensers (which would not be very easy in many cases), for this might readily give rise to the opposite fault, viz., render the action of the condensers imperfect and cause acid vapours to escape from them. The frequent escape of acid vapour within the decomposing-shed is generally proved by the fact that the roof of the shed is very much affected, and that tiles, slates, etc., can be made to stand for some time only by a thick coat of tar.

Another drawback of the decomposing-furnaces worked by hand is the fact that the manufacturer is to a great extent dependent not merely upon the skill, but also upon the goodwill of the men, especially in the case of the pan. If the men lack either the one or the other of those qualities, the consequence will be not merely, as in other processes, the spoiling of a batch, but very frequently the cracking of a pan, with its attendant heavy cost and interruption of work. Also in the case of strikes it is impossible to replace the pan-men by men taken from other occupations, and they frequently trade upon this position.

These considerations have caused several attempts at turning the process of decomposing salt into a mechanical operation, in order, on the one hand, to relieve the workmen from a very disagreeable and unhealthy occupation, and, on the other hand, to make the manufacturer less dependent upon the skill, the goodwill, the whims, and the sobriety of the men. For some time those attempts were not successful, as the apparatus did not resist the simultaneous action of heat and of acid vapours. The first somewhat satisfactory solution of the task was the mechanical saltcake furnace of Jones and Walsh (B. P. 1864; of 1875). This furnace and the results obtained with it and a number of improvements and modifications in construction, have been exactly described and illustrated by diagrams in the first edition of this book, Vol. II., pp. 97 to 106. The furnace possessed a fixed, circular pan of 14 or 16 ft. diameter, with flat bottom and a flange all round, heated from above by a coke fire, from a fireplace arranged on one side; in the centre of the pan a perpendicular iron shaft was made to revolve, with horizontal side-arms and stirring-ploughs. No further description need be given, as the first furnace of Jones and Walsh, in spite of the great praise originally accorded to it, and though thirty such furnaces were really erected (none of them certainly according to the drawings given in the patent specification), had too many faults. The inventors themselves superseded it by a new construction (B. P. 2481, of 1877), in which the fixed pan with revolving stirrers is replaced by a revolving pan with fixed stirrers, as shown in Figs. 43 and 44. The pan A is made of wrought-iron, with a cast-iron lining; it rests on a central footstep, C, which is protected against the action of the chemicals by a collar, D, connected with the pan itself. The circumference of the pan is provided with a collar, E, which dips into a circular fixed spout, F, filled with sand, attached to the brickwork and forming a gas-tight lute during the revolution of the pan. The cogwheels G and H produce the revolution of the pan, whose weight is carried by the pulleys J J, running on the annular rail I, similar to a railway turntable. The pan is covered by an arch whose commencement is visible at K; one side of this has a communication with the laterally arranged fireplace, the other with a flue for taking away the gases. Opposite the former opening the central shaft is fitted at an angle of 60 degrees with two strong arms, L L, to which are attached a number of stirrers (B) or ploughs (M) at equal distances, in such manner that the ploughs of one of the arms work in the interstices left by the ploughs of the other arm, and thus rake up the whole bottom of the pan. The cast-iron lining, provided for protecting the outer wrought-iron pan consists of several segments, connected by a special expansion joint described in the patent.

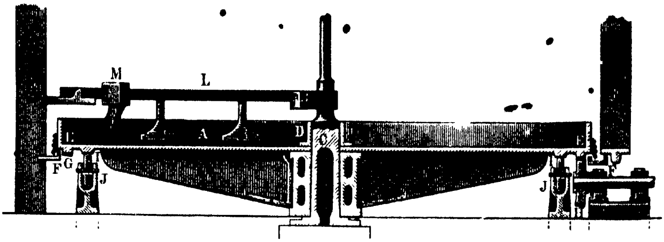

FIG. 43.

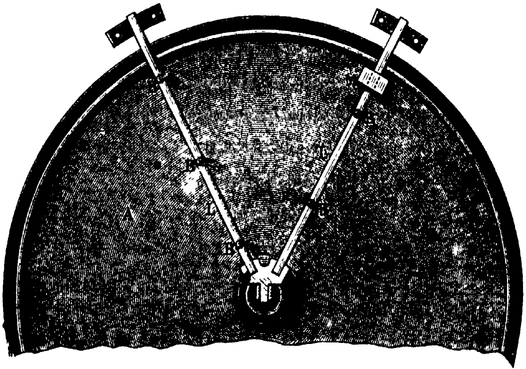

FIG. 44.

The charging of the pan was to take place by means of a movable spout, which was to be lowered in a slanting position at the end of an operation, so that during the revolution the contents of the pan would partly rise up in the spout. This plan evidently did not answer its purpose, for a new patent, No. 976, of 1880, describes another kind of sand lute and a much better discharging-arrangement, which is sufficiently explained by Fig. 45. This new patent also describes another kind of cast-iron stirrer of bent shape, firmly fixed to one side. From later information given by Jones[1] it is seen that this stirrer is placed in such manner as to leave at the pan-bottom a crust of saltcake about 1 inch thick, which affords a good protection to the metal against the acid. The pan thus remains practically untouched, whilst the stirrer must be renewed once every two months.

Fig. 45 shows the more recent form of the Jones furnace, according to a diagram published in the above-mentioned Proceedings, without any accompanying description. The stirrer *a* is seen in the left half, shown in section. Fig. 46 represents half of the pan on an enlarged scale, and gives some details, especially for the feeding of the salt (at *a*) and the acid (at *b*), and the connection of the revolving pan with the fixed brickwork at *c*. Fig. 47 shows that Jones later on adopted, like Mactear, a continuous system of feeding, by means of the conveying-worm *a*; it also shows the fixed stirring-blade *b* and the discharging-scraper *c*. These adjuncts do not seem to be provided in the majority of Jones furnaces actually constructed.

The mechanical construction of the Jones furnace does not seem to be so elaborate as that of the Mactear furnace (which was constructed subsequent to it); at all events it is inferior to the latter as regards the condensation of the hydrochloric acid, which in both cases is intimately mixed with fire-gases; but in the Jones furnace it is given off at first very rapidly, afterwards very slowly, just as in hand-furnaces. It is certainly possible to condense all the acid, but the acid is mostly too weak for sale. In order to effect a complete condensation, the work must be carried on much more slowly than the inventors had assumed, and this naturally involves a larger outlay for fuel, labour, and interest on plant than originally expected.

In spite of its considerable cost and the above-mentioned drawbacks, the various forms of the Jones furnace were speedily adopted by many chemical manufacturers. By 1878 thirty

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[1] *Proc. Soc. Chem. Ind.*, 1881, p. 85.

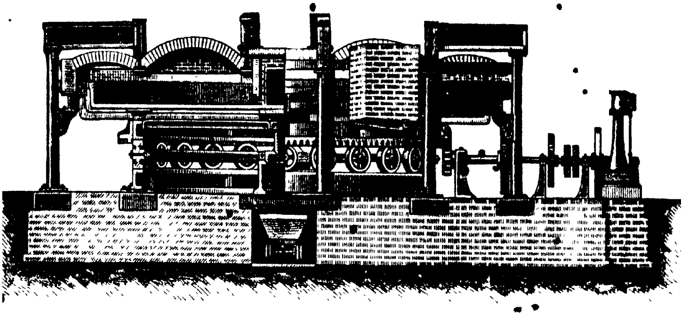

FIG. 45.

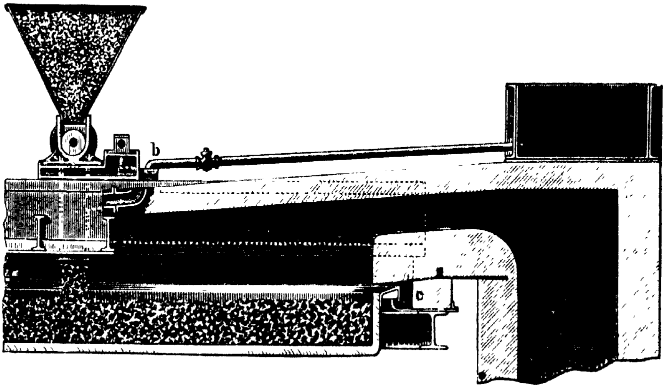

FIG. 46.

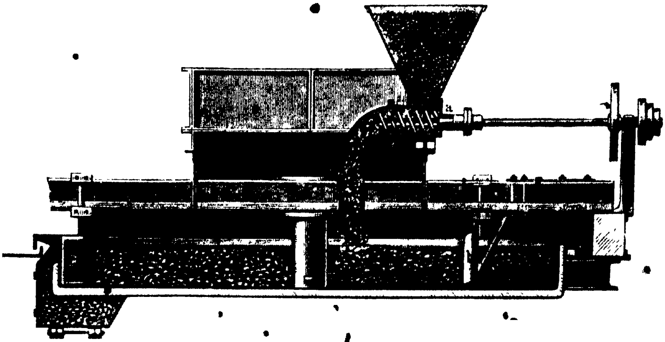

FIG. 47.

furnaces of the older type had been erected, most of which have long been stopped. The second, greatly superior, system was also widely used. It seems to be decidedly better adapted for the manufacture of potassium sulphate, for which it was employed at Messrs Vorster & Grüneberg's, near Cologne. With this furnace it is possible to avoid all nuisance to the neighbourhood, to condense all the hydrochloric acid (although not sufficiently strong), and to make excellent saltcake with 4 per cent. less sulphuric acid than in hand-furnaces (viz., 85·80 per cent. H_2SO_4 to 100 dry NaCl, against 83·76 per cent. H_2SO_4 required by theory). The consumption of coke is stated to be 12½ per cent of the saltcake for sodium sulphate, and 15 per cent. for potassium sulphate. The saving of labour in comparison with the hand-furnace is two-thirds. A furnace of the kind described yields 7½ tons of saltcake in twenty-four hours.

An enormous Jones furnace was erected at Gateshead. The pan is 32 ft. in width; the central pan is 15 ft. in diameter and leaves an outer annular space of 8 ft. 6 in. width with three stirrers forming the working area proper. The firing takes place with Wilson gas-producers. The charge consists of 25 tons of finely ground rock-salt, and can be finished once every twelve hours; the discharging takes twenty-five minutes. The hydrochloric acid runs from the towers 23° to 26° Tw. (measured cold). The cost of such a furnace with six coke-condensers, roofs, gas-producers, etc., amounted to nearly £14,000. The starting of these furnaces is said to have caused great difficulties. The application of the Wilson gas-producers for this purpose has been minutely described in the *J. Soc. Chem. Ind.*, 1883, p. 456. It is there stated that formerly the consumption of coke per ton of saltcake was 6¼ cwt., costing 3s. 9d., together with 4d. for the firemen; with the gas-producers the consumption was 6½ cwt. coal, costing merely 1s. 2d., together with 11d. for labour and steam—that is, about 2s. per ton. [This statement, however, takes no account of the fact that with coal as fuel for open roasters the condensed acid is always much weaker than with coke; *cf.* p. 110.]

Lunge saw some of these giant furnaces at work in 1889, with Wilson producers. The saltcake made tested only 0·1 or 0·2 per cent. NaCl, but the hydrochloric acid tested only 10° Tw.—

a drawback which would not be tolerated under ordinary circumstances.

In 1907 there were three Jones furnaces at work on Tyneside, for the manufacture of saltcake exceptionally free from sodium chloride.

Mactear's saltcake furnace (B. P., 28th Nov. 1879) is shown in Fig. 48 on a scale of $\frac{1}{80}$. It is a revolving furnace, very much on the principle of the carbonating furnace constructed by the same inventor (Chapter XIII.). The frame, *d*, of the pan runs by means of wheels, *n*, on an annular rail. The lute is made by a flange, suspended from the girder *a* bearing the arch, and dipping into a circular spout, *s*, filled with sand, or preferably with ground saltcake. The revolution is effected by a cogwheel attached to the lower side of the pan, moved by the cogwheel *w*, which is driven by the gearing *t*.

The principal peculiarity of this furnace is its continuous central feeding, for which the central cast-iron pan *e* is provided. The remainder of the large pan is lined with fireproof bricks, boiled in tar, and separated from the metal by a special cement, resisting both heat and acid. In this lining there are annular corrugations c^1 c^2 c^3; behind c^3 we find the cast-iron compartment for receiving the finished saltcake. The central pan *e* receives both salt and sulphuric acid continuously in exactly regulated proportions—the acid through pipe *f*, the salt through a worm coming from the hopper *h* and ending above pipe *i*. The salt arrives by a chain of buckets (not shown in the drawing) which runs over pulley *g*, and is moved by the gearing *k* attached to the cogwheels of the stirring-apparatus. The gearing *t*, mentioned above, drives also a cogwheel *u*, which drives four other cogwheels placed in the same plane, and thus carries along the four stirring-blades fixed in frame *b b*. By their action the magma, formed in the central pan *e* and running all over its margin, is worked over whilst passing underneath the blades, and is gradually moved towards the circumference, where it is found to be converted into a dry powder of finished saltcake, and is continuously discharged into compartment *o*, which with its continuations *r*, bent twice at a right angle, connects with the fixed annular spout *p*, and is there luted by sand. This spout leads to the collecting-box *q*, from which the saltcake is removed from time to time.

At both sides of the stirring-apparatus cast-iron partitions are arranged within the space, covered by the pan-arch and

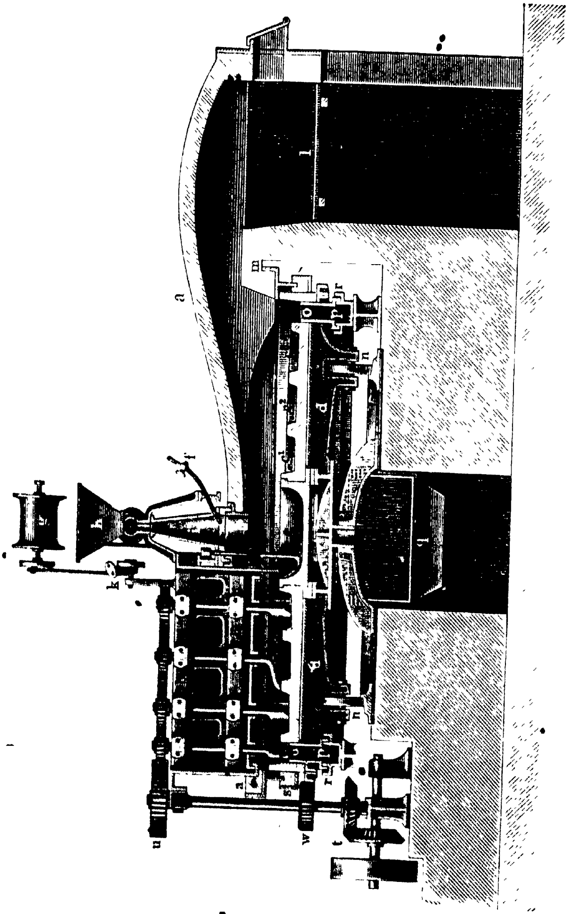

FIG. 48.

pass through the latter, allowing the perpendicular shafts to enter, so that the moving parts are not exposed to the hot acid vapours. These vapours escape through two cast-iron pipes on both sides of this chamber. A later patent (No. 10812, of 1884) gives some improvements in details.

Such a furnace produces on an average 1 ton of saltcake per hour. The condensation of the hydrochloric acid, in spite of its being diluted with fire-gases, is quite perfect (95 per cent. of the theoretical quantity), owing to its continuous evolution. It is stated that, without employing any post-condensers, the acid is stronger than from open roasters, and quite as good as from the best blind roasters, whilst it requires only half the condensing space needed by the latter. But this assertion seems to be exaggerated. It goes without saying that here also there is no escape of acid vapours into the working-shed, that there is a great saving of labour, that the quality of the saltcake is very good, and that rock-salt is as easily worked as pan-salt. Repairs are not so frequently required as with the Jones furnace, which also produces much less.

In Fig. 48 the fireplace is shown as an ordinary fire-grate. In practice, as in the case of the Jones furnace, it is necessary either to burn coke or else employ a well-regulated gas-producer, otherwise the condensers would soon be stopped up with soot.

The saltcake can be easily made to contain less than 0·5 per cent. NaCl and 0·8 free SO_3. Mactear[1] gives the following average [?] analysis of a batch of 35 tons saltcake from his furnace:—97·96 Na_2SO_4, 0·53 H_2SO_4, 0·10 NaCl, 1·16 $CaSO_4$, 0·25 insoluble in water (with 0·09 Fe_2O_3, all insoluble in water, 0·05 coming from the acid and 0·04 from the furnace and the tools). It is equally easy to make saltcake in fine powder for glass-making, or in a denser state, but free from semifused lumps, for black-ash furnaces.

The following analysis of Mactear saltcake is from a private source:—Na_2SO_4, 97·40; NaCl, 0·08; H_2SO_4, 1·00; Fe_2O_3, 0·08; Al_2O_3, 0·06; $CaSO_4$, 0·97; $MgSO_4$, 0·03; insoluble in HCl, 0·02; H_2O, 0·30.

Mactear claims the following advantages for his furnace. Whilst a Tyneside open roaster (as shown pp. 97 *et seq.*) finishes 68 tons of saltcake per week of six days, and requires three men per shift to work it, equal to 11 tons per man per week, the Mactear furnace finishes 144 tons per week of six days, or 72 tons per man per week. In addition to this, for each two or three furnaces, one man is required to look after the engine and machinery. Altogether the actual amount of labour is reduced to one-fourth. The labour cost for Tyne open roasters is 34·76d., for Glasgow blind roasters 35·49d., for Mactear furnaces 14·00d. per ton of saltcake. The fuel required for the latter is 4½ cwt. of coke per ton of saltcake, or an equal quantity of small coal with gas-producers. There is also a saving of 3 per cent. in sulphuric acid [this has been denied by E. Carey]. The following table is interesting as showing the work done by other kinds of furnaces as well. The figures (Lunge's) refer to the cost per ton of saltcake:—

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[1] *Proc. Soc. Chem. Ind.*, i., p. 75.

	Tyne open roasters.		Glasgow close roasters.		Mactear furnaces.	
		s.		s		s.
Wages	.	2·90	. .	2·96	...	1·17
	Cwt		Cwt.		Cwt.	
Coke	4·29 at 10s. 4d.	2·65	10 at 5s. 6d.	2·75	4·50 at 12s.	2·70
Coal	2·40 „ 3s. 5d.					
Steam	. .		...		...	0·50
Repairs		1·50		1·50	.	0·92
Int. and Dep. 20 per cent.		0·50		0·75	. .	0·64
		7·55		7·96		5·93
Deduct 3 per cent. of vitriol saved						1·00
						4·93

This does not include the royalty of 6d. per ton for the Mactear furnace. The statements concerning the latter were attacked as being much too favourable in the discussion following the reading of Mactear's paper (*loc. cit.*, p. 143). Carey states the expense per ton of saltcake with his blind roasters = 2·87s. for labour, 1·4s. for coals (at 4s. per ton), 0·54s. for repairs, and 0·42s. for interest and depreciation; together 5·24s., not 7·96, as calculated by Mactear. We must point out, in justice, that both were interested parties, since Carey was alluding to the Deacon plus-pressure furnace owned by the firm of Gaskell, Deacon & Co., in which he was a partner.

According to a letter received from Mr Mactear in 1882, he then worked his furnace with Wilson gas-producers, and consumed per ton of saltcake 6½ cwt. of very inferior coal at 3s.

per ton. But in the official *French Exhibition Report of* 1891 (p. 72), Lequin, the general manager of the Saint-Gobain works, states that he had to abandon the gas-producers and go back to coke, and that hence the expected saving in fuel had not taken place.

Dr Lunge was privately informed that in a large factory where both kinds of furnace were used, the Mactear furnace was greatly superior to even the most recent kind of Jones furnace in the matter of repairs. Even the Mactear furnace gives some trouble with its bottom, which is best overcome in the following way:—The wrought-iron pan is first covered with a layer of gypsum, then comes a thick sheet of lead, on this again gypsum, and in the latter acid-proof bricks are embedded. The stirrers are not separated from the fire by partitions; they last several weeks, and do not give anything like so much trouble as those in the Jones furnace.

At the Chauny works that stirrer in the Mactear furnace which is nearest to the centre, and therefore yields too much iron to the saltcake, has been replaced by a stoneware stirrer, which is possible, as the mixture is still very thin at that place.

As regards the condensation of the acid, Mactear states that a coke condenser 5 × 5 × 48 ft. suffices for a furnace turning out 30 tons in twenty-four hours—that is, 40 cub. ft. per ton of saltcake in twenty-four hours—whilst the best open roasters require 400 cub. ft., and 210 decomposing furnaces examined in 1867 had an average condensing space of 484 cub. ft. (*cf.* reliable information thereon in Chapter VI.). Post-condensers are not required.[1] According to his circular, even with insufficient preliminary cooling the acid runs off at 25° to 27° Tw. (in a letter to Lunge, Mactear speaks of 24° Tw.), and represents 98 per cent. of the theoretical quantity. There is absolutely no "low-level escape" even during discharging. The repairs amount to only 8d per ton, less than with hand-furnaces for the pans alone. It has been already pointed out that the saltcake is very good, and that rock-salt is worked as easily or even better than pan-salt (p. 55). Taking into account that the Mactear furnaces require much less condensing space, floor space, and roofing, even the prime cost of plant is stated to be below that of hand-furnaces.

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[1] Carey stated in the discussion that the above figures are much too high; his firm has only 150 cub. ft. of condensing space, and post-condensers have been entirely abandoned in Lancashire.

In the *Paris Exhibition Report* (*cf.* p. 201), Lequin states that at Chauny extremely large condensing apparatus was provided for the gases from Mactear furnaces (to be described in Chapter VII.), but that the acid only got up to 28° Tw., whilst some English works only get up to 21°. In order to get up to the strength of 33° Tw. required for commercial acid in France, it was necessary to make some extra strong acid in iron cylinders, and to charge the saltcake from these in the Mactear furnace, which causes much expense.

Formerly in France, as well as in England, many Mactear furnaces had been provided with Wilson gas-producers, but these have been again replaced by coke fires, probably because the difficulty of making strong acid was too great in the former case (*cf.* p. 138, with reference to the Jones furnaces).

In spite of its high cost (£2000 for the furnace alone), the Mactear furnace was widely introduced in the larger alkali-works. Nowadays this would hardly be the case, as it labours under the same drawback as the Jones furnace, viz., that the hydrochloric acid cannot be made strong enough—a drawback which is inseparable from the principle of driving out the whole of the acid by open fire; hence the fact, mentioned on p. 119, from the *Alkali Inspectors' Reports*, that the works fitted up with mechanical furnaces, in spite of the large sums invested in these, were gradually replacing them by hand-worked plus-pressure furnaces, in order to increase the yield of strong acid. To this we must add the expense for fuel, as in 1889, for example, coke cost on the Tyne 9s., but coals only 3s. 6d. per ton. In Bristol in 1907 three Mactear furnaces were still at work, but these took the half-finished saltcake from the ordinary pots and only did the calcining work.

At the present time, the tendency is again towards the introduction of mechanical furnaces, for a variety of reasons. The difference in cost of coke and coal has diminished, the cost of labour has very greatly increased, and various improvements have been introduced in the details of the mechanical furnaces.

Other Mechanical Furnaces.—Newall (B. P. 2417, of 1880) proposes to make decomposing-pans of phosphorous bronze, with a double bottom, heated by steam or hot air, in order to get the mechanically stirred mixture of salt and sulphuric acid up to 120°. If the decomposition is to be finished in the pans themselves, the mixture must ultimately be brought to 350° C.

Herman (B. P. 13983, of 1887) proposes discharging the saltcake from mechanical pans by means of a moving chain band.

A number of inventors have tried to avoid the greatest drawback of the previous mechanical furnaces, viz., the mixture of the whole of the acid vapours with the fire-gases.

A patent of Black and Hill (dated 14th June 1877) is intended to avoid this, by reverting to the principle of carrying on the operation of decomposing in two separate stages. The pan heated from above and provided with revolving stirrers is essentially retained, but only that function is left to it which belongs to the calcining furnace or roaster of the ordinary process. The first action of the sulphuric acid on the salt takes place in a special apparatus, also provided with stirring-gear, but heated from below like an ordinary decomposing-pan. This furnace is illustrated and described in our first edition, Vol. II., pp. 107 to 110, but it has been replaced at the inventors' works by the newer construction of Black and Larkin, described below. A further step was taken by Cammack and Walker (B. P. 3rd March 1876), whose furnace (illustrated and described in our first edition, pp. 110 to 114) consisted of a cast-iron tube, 3 or 4 ft. wide, into which at one end salt and sulphuric acid was continuously fed, and was moved along the tube, so that finished saltcake was discharged at the other end, and the HCl was continuously given off in an entirely uniform stream. This altogether avoids the necessity of open firing, and causes the whole of the HCl to escape in a concentrated state and quite uniformly during the whole time of working. This very interesting furnace was erected by Messrs Golding & Davis at Widnes, but was soon stopped, because the mechanical difficulties could not be overcome. The two shafts inside the cylinders, for which no intermediate bearings can be provided, soon sagged under the influence of the heat. Owing to this the teeth and scrapers did not work properly, and the mixture, instead of moving evenly along the cylinder, stuck fast to the sides of the cylinder and stopped it up. As this furnace would be extremely favourable for Deacon's chlorine process, his firm took it up, but soon abandoned it, and we must therefore refer to the description of it in our first edition.

Hazlehurst's furnace (B. P. 509, of 1882) consists of a decomposing retort, turning on horizontal hollow trunnions; through one of these the sulphuric acid is introduced, through the other the HCl escapes; the heating takes place from below. Within the retort, near the top, scrapers are attached to a rod fixed to one of the trunnions, for keeping the sides clean. (There can be no doubt that this apparatus will not answer in the long run.)

Mackenzie (B. P. 304, of 1883, not sealed) proposes connecting a series of retorts, through which the materials pass in succession.

Walker's furnace (B. P. 9760, of 1887) resembles that of Cammack and Walker, but differs from it by providing two revolving cylinders with agitating gear, the lower of which receives the mixture from the higher one in order to finish it. It is unlikely that this furnace has ever been constructed.

The only mechanical furnace which has been approved by a practice of some duration, besides those of Jones and Mactear, is an invention of Larkin's (Black and Larkin's patent, 4718, of 1884), and is shown in Figs. 49 to 51. It is a combination of an ordinary decomposing-pan of the type described on pp. 86 *et seq.*, with a circular muffle, provided with a mechanical stirrer. The furnace-bottom *a* consists of earthenware or iron slabs and rests on dwarf walls forming the partitions of the fire-flues. In the centre there is an iron pipe, *b*, with an outer protecting pipe, b_0, made of stoneware; this pipe passes through the furnace-bottom and the flue below, and serves for protecting the agitating-shaft *c*. A number of small fires, one of which is visible at *d*, are arranged at one end of the furnace, and serve for heating the bottom of the muffle, the top of which is heated by another row of fires at the opposite end, at *e*. The muffle is very low and its cover is formed of metal plates, resting on H-shaped iron girders, *g g*, which at the same time serve as partitions for the flues The interior of the muffle is accessible by working-doors, a^2, which serve for discharging. The charging takes place from the top through pipe *h*, which comes from the decomposing-pan *i*, with the gas-pipe *l*. The pan can be heated by the waste heat from the muffle-fires. The acid vapours escape at the side of the muffle through pipe *j*, without mixing with fire-gases. The agitating gear consists of the shaft c with horizontal arms c_2, to which are attached the

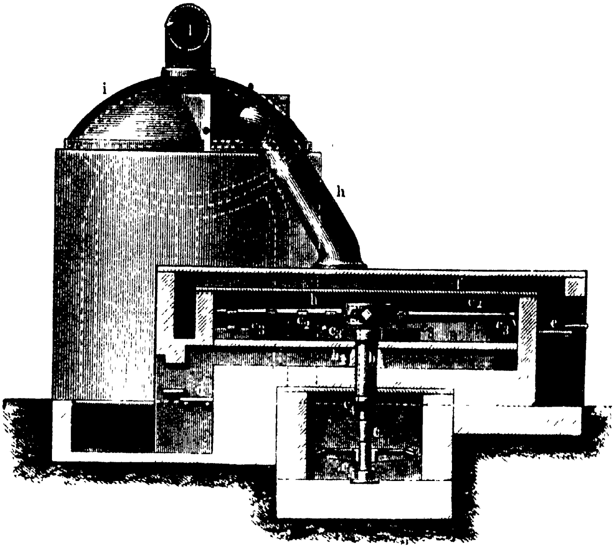

FIG. 49.

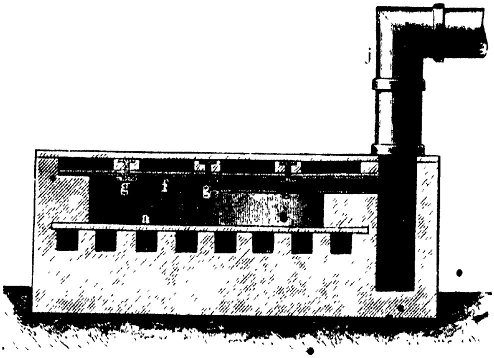

FIG. 50.

scrapers c_3 The shaft is provided at its lower end with the sand-lute c_4, which keeps out the air, and is protected against the acid vapours by the pipes *h* b_2. It is steadied at the top by means of a bracket fixed to one of the girders *g*, and below by the footstop c_5. The small flues from *d* and *e* combine into a main flue; the firing takes place on the plus-pressure plan (p. 114 *et seq.*), in order to render any leaks of the muffle harmless.

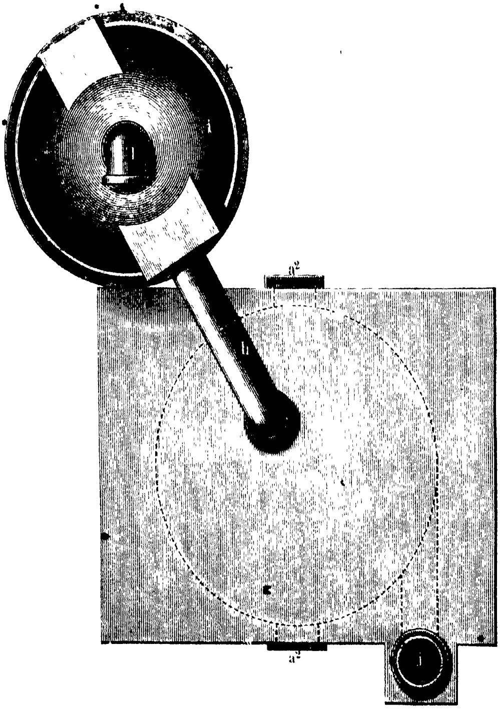

FIG. 51.

We take the following further details from a paper of Rennoldson[1]:—The moving parts are very strong where this is requisite, but not unnecessarily heavy where this is not called for. The replacing of one large fireplace by many small ones, each of them provided with a separate damper and very easy to manage, is of extreme importance for attaining a uniform heating of the muffle. The fire strikes directly from the front to the back, without having to travel backwards and forwards; hence very little draught is required, and the plus-pressure system is easily carried out. The application of a close muffle with mechanical agitator unites the advantages of all systems: excellent decomposition without manual labour, avoidance of any low-level escape from the (closed) doors, complete condensation of HCl without post-condensers, and production of the strongest hydrochloric acid. As the muffle-doors remain closed during the work, and no false air can get in, much more draught than usual can be given in the condensers, which is very desirable even for the pan *i*. Rennoldson gives the following results of three months' work with three Black and Larkin furnaces:—

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[1] *J. Soc. Chem. Ind.*, 1885, p. 316.

Salt decomposed, on an average, per furnace in a week of six days	78 tons.
Sulphuric acid consumed on damp salt	78 per cent.
Yield of saltcake	110 „
Percentage of SO_3 in the saltcake	0·4 „
Percentage of NaCl in the saltcake	1·3 „
Temperature of gas from pan and roaster at the condenser inlet	79·5° C.
Test of gas from pan and roaster at the condenser outlet, per cubic foot	0·19 grain.
Ditto in chimney	0·7 „
Test of hydrochloric acid produced	29° Tw. at 15·5° C.
Bleaching obtained, 1 ton from each	46 cwt. salt.
Labour per ton of saltcake (formerly 2s.)	1s. 9d.
Steam (fuel and labour for)	0s. 1¾d.
Fuel for pan and roaster, 7½ cwt. small coal	1s. 3d.

The repairs during fourteen months were practically *nil;* only the scrapers had to be replaced.

In the discussion T. W. Stuart, one of the most competent judges, pointed out that the Black and Larkin furnace as regards the production of chlorine equals the Jones and Mactear furnaces, and is superior to the Deacon furnace; the small saving of wages (about 10d. per ton of saltcake) against the latter will be partly, at least, covered by the extra repairs. Its essential advantages are that of a really efficient machine over hand labour, the complete removal of the low-level nuisance, more complete condensation, combined with great durability. According to the *Alkali Inspectors' Report,* two such furnaces were erected in 1890, which seems to prove their efficiency. It must, however, not be overlooked that the Black and Larkin furnace does not abolish hand labour for the decomposing-pan, and thus does not satisfy that need which first led to the invention of mechanical furnaces, but only solves a much less important problem, that of mechanical work in the second stage of the process.

Recent Mechanical Saltcake-furnaces.

Thomson and Worsley (B. Ps. 21945 and 21946, of 1894) employ two decomposing-pots to each roasting-furnace. These pots are fitted with stirrers and automatic charging-apparatus, by which the supplies of salt and sulphuric acid are regulated so as to keep the vitriol in excess. The charge, which remains sufficiently liquid, flows through a pipe above the level of the agitator into the roasting-furnace. This is a round muffle-furnace, heated above and below, the revolving top carrying stirrers and ploughs, which mix and gradually move the charge towards the outlet, where it is continuously and automatically discharged. As the charge passes from the pot into the furnace, more salt is added by a conveyer-worm, in proportion to the excess of acid in the pot. Thus a continuous stream of hydrochloric acid is evolved, nearly free from water-vapour, and fit for the manufacture of chlorine by the Deacon process without further drying.

Hart (Amer. P. 698704, of 1902) forces the mixture of common salt and sulphuric acid continuously by means of steam into a revolving cylinder, heated just below a red heat.

The Maschinenbauanstalt Humboldt (B. P. 27061, of 1906) avoids certain drawbacks by constructing every stirrer as a two-armed lever, and supporting it on the shaft in such manner that the revolving tendencies of each two diametrically opposed stirrers neutralise each other.

The mechanical furnace of the Mannheim Verein Chemischer Fabriken (Ger. P. 137906) is essentially intended for working up nitre-cake, and will be described in Chapter V.

K. Oehler and Anilin und Anilinfarbenfabrik (Ger. P. 165099, of 1904) have patented a muffle-furnace which communicates on the one hand, through openings in the bottom, with a channel running underneath the whole length of the furnace, for the purpose of removing the sulphate, and on the other hand, through two sets of adjustable openings in the roof, with an auxiliary condensing plant. When the hot sulphate is being removed from the furnace, the acid vapours are drawn through the auxiliary condensing plant.

With a view particularly to obviating the escape of obnoxious vapours, K. Oehler (Fr. P. 354467, of 1905) describes a closed muffle in which the charge is heated, and from which the acid vapours are conducted away for condensation without access of air, into a receiver in which the gas meets with an excess of moisture. The floor of the muffle is provided, near the working doors, with traps through which the sodium sulphate is discharged into a channel beneath, from which it is conveyed by an endless chain into a closed receptacle in which cooling is effected. As the discharge takes place, communication is opened to a tuyère leading to a secondary condensing arrangement, and opening into the roof of the muffle, close to the door from which unabsorbed gases are drawn through the action of diminished pressure, thus avoiding escape into the air of acid vapours. The system of pipes, with their connections and means for directing the gases as required are shown in the patent specification. (Compare Fr. P. 318386 of 4th Feb. 1902; also B. P. 2856 of same date.)

Another form of saltcake-furnace has been patented by J. H. Neild, Assignor to General Chemical Company, New York (U.S. P. 1033825, of 1912).

Chem. Fabr. Rhenania, C. Thelen, and F. Wolf (Ger. P. 279997, of 1913) heat the charge in a pear-shaped "pan" mounted horizontally and provided with a screw agitator, and then, by rotating the screw in the opposite direction, force the charge rapidly through an opening in the narrow end of the pan into the roaster. The material is delivered on to the circular muffle-hearth of the roaster at the centre and is moved across the hearth by mechanical scrapers to a discharge opening at the periphery.

YIELDS AND COSTS.

The *yield of saltcake* from the salt decomposed depends on the quality of the salt and the care of the men. Pure NaCl would theoretically yield 121·45 per cent. of Na_2SO_4. Salt with

7 per cent. moisture (the other impurities remain in the product) 112·9 per cent. of saltcake. The loss by absorption in the furnace-bed, spilling, etc., can only amount to a small percentage. In England, when employing common salt containing 6 to 8 per cent. moisture, a yield of at least 110 per cent. saltcake is expected.

The statements of the Belgian Commission, according to which some works only obtained 109, 108, and 102 parts respectively of saltcake from 100 of common salt, prove either an error in the figures (especially for the last case) or extremely careless working. Chandelon reports[1] the result of exact trials with three furnaces at Risle, where from 2700 kg. salt, containing 2432 kg. NaCl, 3113 kg. saltcake (= 115 per cent.) were obtained, but it is not stated how much of the 278 kg. of the crude salt present otherwise than as NaCl consisted of moisture and how much of other impurities. At a Rhenish works the regular yield is stated at 119 per cent. of the salt, which even with dry salt seems extraordinarily high; 116 to 117 per cent. is generally considered very satisfactory. The yield from the very pure salt of Neu Stassfurt, which regularly tests 99 per cent. of NaCl, is actually 120 per cent.

It is quite usual in England to refer the yield of saltcake directly to the pyrites consumed, so as to be independent of the estimation of the sulphuric acid produced, which certainly can in no case be called altogether trustworthy. In this way the difference between open and blind roasters as to their consumption of sulphuric acid becomes very clear. In the best works on the Tyne (all of them working with open roasters) 100 parts of 48 per-cent. pyrites only yield 175 to 178 parts of 97 per cent. saltcake; 185 may be called the maximum. The true average yield in the best works is, upon 100 parts of sulphur charged into the kilns (not actually burnt), about 380 parts of saltcake, or, assuming that 4 per cent. of sulphur is left in the cinders (= 3 per cent. of the sulphur in the pyrites), on 100 parts of sulphur actually burnt, 405 parts of saltcake. In Lancashire, with *blind roasters*, it is asserted that 195 to 200 parts of saltcake are got from 100 pyrites. In most, if not in all cases, this assertion undoubtedly rests either upon self-deception or upon the fact that very poor saltcake is made; it would correspond to 406 to 417 saltcake per 100 of sulphur charged, or 433 to 444 saltcake upon the sulphur actually burnt. In a factory acknowledged to be one of the best-managed in all England, only 430 parts of 97 per-cent. saltcake are obtained upon 100 parts of sulphur actually burnt. This certainly is 6 per cent. more than the above-mentioned yield with open roasters. From the figures of a celebrated French works, fully authenticated by Lunge, a yield of only 405 parts of saltcake per 100 parts of sulphur is obtained, and that with *blind* roasters—that is, no more than good English works obtain with *open* roasters. Probably there was in this case a larger loss in the manufacture of sulphuric acid.

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[1] *Bull. Soc. d'Enc.*, 1871, p. 323.

On the *loss of sulphuric acid* in the manufacture of saltcake, Wright[1] has given some figures which, nowadays, must be considered as obsolete. Grossmann[2] enumerates the following sources of loss:—Volatilisation of sulphuric acid from the roaster and condensation with the HCl; mechanical carrying away of saltcake with the HCl; so-called "free acid" in the saltcake; escape of SO_2 from the roaster; formation of sulphates from other bases present in the salt as impurities. On an average, he found that of 100 parts of sulphuric acid employed in close roasters there was lost:—

As "free acid" in the saltcake	0·7 parts
„ sulphuric acid and sulphates in the hydrochloric acid	1·6 „
„ SO_2	0·3 „
„ other sulphates (with English pan-salt)	...
	2·6 parts

The loss of sulphuric acid in open roasters may be taken as 5 per cent. (Hurter confirmed Grossmann's figures, but Muspratt declared them to be too low.)

Costs.

For the manual labour in decomposing, in England one man per shift is required for the pan, and he has also to wheel the salt and coals and to run the acid; for the roaster usually two men are employed, who have also to wheel away the saltcake. If less than 8 cwt of salt are decomposed per hour, only one roaster-man is needed. Consequently with blind roasters three men in twelve hours make about five batches of 15 cwt. of salt, = 4 tons 3 cwt. of sulphate; with open roasters usually twelve charges of 8 to 10, or even 10½ cwt. of salt, = 5 tons 6 cwt. to 6 tons 12 cwt., or 6 tons 18¾ cwt. of saltcake. They are always paid according to the quantity of saltcake got out. With mechanical furnaces the labour, of course, is much less (pp. 140 and 144).

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[1] *Chem. News*, xvi., p. 17.

[2] *J. Soc. Chem. Ind.*, 1882, p. 135.

The consumption of coal for the pan at a good English works over a long period of time was stated to Lunge at 15·1 lb., that of coke for the open roaster at 23 lb. per 100 lb. of saltcake. Lunge himself required a good deal less, viz., only 12 lb. of coal and 14·3 lb. of coke, probably because the work was not pushed quite so hard. No numerical statements from works where blind roasters are employed and the pans are fired separately can be given. The statements respecting works with blind roasters and the pans fired by the waste heat of these are very contradictory; a German works states its consumption of coal at 34, a French one at 28 to 32, another French one at 46 parts of coal to 100 parts of saltcake. According to the *Belgian Report of* 1855 (p. 63), the Moustier works averaged 120 kg. of coal to 300 kg. salt—that is, 37 parts to 100 parts of saltcake; the Risle works, 133 coal to 351 salt—that is, 35 coal to 100 saltcake. For further statements on the amount of fuel consumed, see pp. 144 and 151.

In the second edition of this book (Vol. II., pp. 229-32) detailed statements on the cost of saltcake at Belgian works, by Chandelon, are quoted which we will not repeat, as they refer to a remote period (1864), as well as the figures of Kopp, from a French works in 1866. The following is a statement, from the result of a normal year (1875) in Lunge's experience, of the cost for saltcake made with *open roasters:* 1000 kg. of saltcake required—

913 kg. salt with 5 per cent. moisture, at 14s.	£0	12	9·4
959 „ sulphuric acid at 144° Tw., at 28s.	1	6	10·2
160 „ coal, at 5s.	0	0	9·6
195 „ coke, at 14s.	0	2	8·8
Wages	0	4	3
Repairs (exclusive of broken pans)	0	1	3
Average cost of broken pans	0	0	5
	£2	9	1

The requisite quantities, etc., starting directly from pyrites, were:—

591 kg. pyrites, at 48 per cent. sulphur.
11·3 „ nitrate of soda.
913 „ salt.
370 „ coal and 195 coke.
Wages, 7s. 3¼d.
Repairs (inclusive of the renewal of chambers), 2s. / 2d.

In none of these cost-accounts is the value of the hydrochloric acid, obtained as a by-product, reckoned.

At several factories on the Tyne it is asserted that they require only 540 parts of pyrites for 1000 parts of 97 per cent. saltcake; at others in Lancashire the amount stated is only 513 parts of pyrites (details on p. 154); but since, as a rule, statements of yields are very unreliable, and every manager represents his results in the most flattering light, such statements cannot be implicitly accepted, and it is preferable to base the costs upon much less favourable data. Theoretically, 1000 parts of 97 per cent. saltcake would only require 218 parts of sulphur or 455 parts of 48 per cent. pyrites; the loss of about 20 per cent. of sulphur is to be accounted for partly by the residual sulphur in the burnt ore, partly (but to a very slight extent) by a loss of gas in the chamber process, and partly (to a much greater extent) by the excess of sulphuric acid employed in decomposing the salt.

The following statements were taken from the books of a Continental works, where saltcake was made in lead pans and calcined in open furnaces, fired with coke. The lead pans were from 7 to 8 ft. long, 5 ft. wide, and 18 in. deep; thickness of lead ⅝ in. Each pan and furnace turned out 2½ tons of saltcake in twenty-four hours, in six batches, the men working 12-hour shifts (at 3 frs. per shift). The acid gases from the pan passed through thirty earthenware receivers of 40 galls. each, those from the furnaces through four stone cisterns, and the combined gases finally through a coke-tower, 40 ft. high, from which the acid issued with a specific gravity of 21½° to 25° Tw.; from the receivers it issued at 32° Tw. The yield from 100 parts moist salt (with 8 to 10 per cent. water) was 108 parts of 97 per cent. saltcake and from 125 to 130 parts hydrochloric acid 32° Tw.

The *cost* of 100 kg. saltcake was :—

	1890			1891.		
	Quantity	Price per ton	Amount	Quantity	Price per ton	Amount.
	kg	fr	fr	kg	fr.	fr.
Common salt (damp) .	90·70	14·66	1·33	92·76	14·66	1·36
Sulphuric acid (140° Tw.)	92·74	32·50	3·01	94·83	32·50	3·08
Coal	19·15	15·15	0·29	17·36	15·55	0·27
Coke	19·43	30·55	0·59	20·19	26·00	0·52
Wages		.	0·47	...	...	0·44
Repairs		.	0·45	.	.	0·45
General expenses . .		.	0·60	.	. .	0·60
			6·74			6·72
Deduct — Hydrochl. acid (32° Tw.)	125	21·50	2·68	128	21·50	2·75
			4·06			3·97

Thermochemistry of the Reactions.

The following is a theoretical account of the thermal changes taking place in the manufacture of sodium sulphate.[1] The first stage, the formation of bisulphate, shows the following heat-values (in kilo-calories) :—

$$\begin{array}{ccccccc} NaCl & + & H_2SO_4 & = & NaHSO_4 & + & HCl \\ +97{\cdot}7 & & +192{\cdot}9 & & +267{\cdot}8 & & +22{\cdot}0 \end{array}$$

The final result is $-0{\cdot}8$ K, which is so small a figure as to be almost within the limits of experimental error. In the formation of neutral sodium sulphate the complete reaction is endothermic, though not markedly so :—

$$\begin{array}{ccccccc} 2NaCl & + & H_2SO_4 & = & Na_2SO_4 & + & 2HCl \\ +195{\cdot}4 & & +192{\cdot}9 & & +328{\cdot}5 & & +44{\cdot}0 \end{array}$$

the result being $-15{\cdot}8$ kilo-cals. As a matter of fact, the mixture must be heated to finish the reaction.

For calculating the total heat required in the saltcake furnace we assume that the 98 kg. H_2SO_4, employed for converting 117 kg. NaCl into 142 kg. Na_2SO_4, contains 30 kg. H_2O ; also that the hydrogen chloride on an average has to be heated to 400° C., the steam to 500°, and the saltcake to 600°

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[1] Fischer, in *Z. anorg. Chem.*, 1888, p. 550.

(the latter is rather too low). The specific heat of sodium sulphate is = 0·232, that of HCl = 0·19, the heat-units required for converting 1 kg. H_2O at 17° into steam at 500° = 812. The calculation is then as follows:—

		K.
Heating the saltcake	142 × 0·232 × 600	19,766
„ HCl	73 × 0·19 × 400	5,548
„ steam	812 × 30	24,360
Chemical work as above		15,800
Mechanical work of evolution of gas (estimated)		526
		66,000

Of course, such theoretical calculations can only serve as guidance for calculations founded on analyses and direct observations of temperature; but the above is probably somewhat near the truth, as both the initial and the final products are not complicated and are comparatively pure. We thus find the amount of heat theoretically required for making 142 kg. of Na_2SO_4 = 66,000 K., or for a metric ton = 457,750 K. Taking the heat produced by the combustion of coal or coke = 7000 K. per kilogram, the production of a ton of saltcake (1000 kg.) ought not to use more than 65·4 kg. of fuel. In reality, however, *at least* 250, and sometimes nearly 400, kg. of coal or coke is burned—that is, never less than four times the theoretical quantity. Even under the most favourable conditions three-fourths of the fuel is lost by radiation from the apparatus and in the chimney-gases.

It may be of interest to consider also the amount of heat (certainly inconsiderable in comparison with the other factors) which corresponds to the work performed in the evolution of gases *in overcoming the pressure of atmospheric air.* Taking the atmospheric pressure at 760 mm. = 10,336 kg. per square metre, and the mechanical equivalent of heat = 425 metre-kilograms, the expansion of gas by 1 cbm. requires $\frac{10{,}336}{425} = 24·3$ K. Since the volume of a kilogram-molecule of all gases is 22·3 cbm., the consumption of heat at 0° for liberating 22·3 cbm., or a kilogram-molecule of any gas, is $22·3 \times 24·3 = 542$ K. and at $t°$, $542\ (1 + 0·00367\ t)$ K., for instance at 20° C., 582 K. Applied to HCl this is, for 2HCl, $2 \times 582 = 1164$ K.; but as this energy is partly supplied by the chimney draught, we have only assumed 526 K. for this work in the above calculation.

The *temperatures* in saltcake muffles have been measured by Schüler[1] with Seger's cones. He found them = 1100° to 1200° C. in the hottest part of the furnace-bed, where the gases from the flues below ascend to the upper part. But these measurements have but little value, as the important point is the temperature *inside* the muffle, and it is apparent that this in the hottest place must not exceed the melting-point of ordinary saltcake, *i.e.*, 800° C.

PROPERTIES OF COMMERCIAL SALTCAKE.

The *saltcake of trade* is a more or less finely granulated mass often containing larger lumps of melted substance. These lumps are always to be suspected of containing a high percentage of sodium chloride, and often entirely consist of this internally. The finer grain a saltcake possesses, the better it is on the whole. Its colour when hot, as it is drawn out of the furnace, is a bright lemon-yellow—if very rich in free acid, even brownish; if much iron is present, brownish red. In the cold it is yellowish or greenish white, often pure white. A dirty grey colour and a granular fritted consistence show that the decomposition of the common salt is incomplete.

The analyses given below and on p. 161 show the composition of commercial sulphate.[2]

The following analyses by Theilkuhl (from Knapp, ii., p. 396) show the "free acid" as acid sulphate:—

	From Nienburg.	?	From Lüneburg.	From Oker.*
SO_4Na_2	96·2	93·3	90·5	65·0
SO_4NaH	0·5	2·4	8·0	31·8
NaCl	1·5	2·9	0·03	.
$Fe_2(SO_4)_3$	0·5	0·5	1·3	1·6
Sand	0.5	0·3	0·1	0·2
Moisture	0·8	0·8	1·1	0·4

* That from Oker is evidently nitre-cake.

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[1] *Z. angew. Chem.*, 1897, p. 361.

[2] *Cf.* the analytical processes, pp. 60 *et seq.*

	I.			II.	III	IV	V	VI	VII	VIII	IX	X	XI.
	Chandelon.			Brown. English.	Theilkuhl and Linden.	Muspratt. (Liverpool).	De Koninck	Tate. English.	Simmonds. English.	Plunkett. Hargreaves's sulphate	Davis		
	English	Belgian.											
	Made in iron	Made in iron	Made in lead.								From a blind roaster.	From an open roaster	Made by Hargreaves's process.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent.	Per cent	Per cent	Per cent
Na_2SO_4 .	93·15	94·10	95·29	96·22	93·1	93·515	93·36	95·25	96·50	99·24	94·393	96·137	97·824
$CaSO_4$ . .	1·21	0·84	0·86	0·97		09·23	1·16	1·25	1·00		1·139	1·148	1·046
$MgSO_4$.	...	0·35	0·77	0·29									
$Al_2(SO_4)_3$.	0·15	0·16	0·41	...					..				...
$FeSO_4$.	0·75	0·97	0·14	0·23	0·4 (Fe_2O_3)	0·191 (Fe_2O_3)	0·42 $(Fe_2O_3$ $+ Al_2O_3)$	0·50 $(Fe_2O_3$ $+ SiO_2)$	0·30 (Fe_2O_3)		0·682	0·558	0·522
$PbSO_4$.	...		0·05	..	..	..			...				
NaCl . .	1·66	0·14	0·37	1·09	0·6	1·345	2·04	1·75	0·75	0·08	2·632	0·234	0·744
SO_3 . .	1·44	2·52	1·30	0·88	..	0·616	1·36	1·00	1·00 (+HCl)	0·20	0·955	1·820	0·022
H_2O . .	1·28	0·48	0·29	...	4·5	0·187	1·45	0·25	0·20		0·087	...	...
Insoluble (sand) .	0·26	0·42	0·51	0·31	0·3	0·130	0·21	.	0·25	0·48 $(+Fe_2O_3)$	0·112	0·073	0·042

I. From *Monit. Scient.*, 1864, p. 51.
II. and III. „ Knapp's *Chem. Tech.*, ii., p. 395.
IV. „ Muspratt's *Chem.*, ii., p. 913.
V. „ Stohmann-Kerl's *Chem.*, v., p. 300.
VI. From *Chem. News*, xxix., p. 144.
VII. „ *Chem. News*, xxix., p. 184.
VIII. „ *Dingl. polyt. J.*, ccxviii., p. 425.
IX.-XI. „ *Chem. News*, xxxii., p. 174.

For ordinary practice usually only the undecomposed sa and the "free acid" are estimated; the latter is expressed a SO_3, but is, of course, in reality present as acid sulphat (*cf.* p. 29). The buyers or users of saltcake are now much mor particular than formerly. Whilst formerly saltcake with 1 pe cent. NaCl and 2 per cent. SO_3 was not found fault wit nowadays well-conducted works supply it always *below* 0·5 NaC and 1·0 SO_3; with good salt an average of 0·3 NaCl and 0· SO_3 can be obtained.

For glass-making purposes the *iron* is also of importanc Ost[1] found, in eight samples of saltcake made by the ordinar process in iron decomposing-pots, from 0·066 to 0·130 per cen iron; in three samples made in lead pans, from 0·009 to 0·02 per cent. iron. All of these are from German works (of whic twenty-four decompose salt for the manufacture of saltcake The plate-glass works require a guarantee that the iron doe not exceed 0·05 per cent.

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[1] *Z. angew. Chem.*, 1896, p. 9.

CHAPTER IV

VARIOUS METHODS FOR THE MANUFACTURE OF SULPHATE OF SODA

A. *Manufacture of Saltcake as a Principal Product from Common Salt.*

THE following processes have been proposed for making sulphate of soda as a principal product from common salt:—

1. *Heating Common Salt with Sulphuric Acid.*—This is the process generally employed, which has been described in detail in Chapter III.

2. *Heating Common Salt with Sulphurous Acid and Atmospheric Air.*—This is the process of Hargreaves and Robinson, described in detail in Chapter V.

3. *Heating Common Salt with Metallic Sulphides, especially Iron- and Copper-pyrites* (Longmaid's process).—The idea of making sodium sulphate by roasting common salt with pyrites is a very old one; Berzelius[1] mentions it as a proposal, with the addition of powdered coal. The fact that pyrites, or brown coal containing pyrites, under these circumstances, yields sodium sulphate on lixiviation, must have been already known in the eighteenth century; for the French Commission of 1792, in their official Report, recommended this mode of preparation as preferable to that proposed by Leblanc.[2] This judgment certainly was proved to be incorrect in practice, and the process was probably never carried out to any extent on a large scale. But attention was drawn to the fact that in the roasting of metallic sulphides with common salt, as in metallurgical processes, a large portion of the sulphur is found in the calcined mass as sodium sulphate; and Glauber's salt derived from this source

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[1] *Lehrbuch der Chemie*, 1836, vol. iv., p. 153.

[2] *Wagner's Jahresber.*, 1857, p. 103.

was actually sent into the market. This may have been the occasion of Longmaid's bringing out a renewal of this process, which was carried on energetically for a number of years and attracted great attention, but in the end had to be given up. His first patent dates from 20th October 1842; a second one of 1st January 1844 makes no essential addition. He proposed to treat metallic sulphides with common salt, in the proportion of at least 60 NaCl to 40 sulphur, in a reverberatory furnace with four beds, each of which is a little higher than that nearer the fire. The mixture is charged upon the highest bed and gradually brought down. The product on lixiviation furnishes sodium sulphate, common salt, and copper salts. The copper is precipitated by metallic iron, the iron salts precipitated by lime, and the sodium sulphate obtained from the mother-liquor by evaporation. The access of air during the roasting must be exactly regulated for each part of the furnace, so that at first only ferric sulphate is formed, from which at a higher temperature, sulphuric anhydride is liberated; this with common salt yields sodium sulphate, free chlorine, and sulphurous acid, but very little of the latter in the presence of air. The following reactions may take place in the presence of air:—

$$2FeS_2 + 8NaCl + 16O = 4Na_2SO_4 + Fe_2Cl_6 + 2Cl$$
$$2FeS_2 + 8NaCl + 19O = 4Na_2SO_4 + Fe_2O_3 + 8Cl;$$

or, in the presence of steam,

$$2FeS_2 + 8NaCl + 4H_2O + 15O = 4Na_2SO_4 + Fe_2O_3 + 8HCl.$$

The latter reaction is only a secondary one in the original process of Longmaid. It is, however, much more complete than the former, and therefore in Hargreaves's process steam is always employed. The addition of small coal frequently made (not by Longmaid) only serves as fuel, and is not only unnecessary, since no great heat is required, but even injurious, by reducing sulphate to sulphide.

By being only gradually moved from the coolest to the hottest part of the reverberatory furnace, the common salt is gradually transformed into sulphate, and the mixture becomes more capable of withstanding a high temperature without melting. This easy fusibility of the mass is just one of the principal difficulties of the process, because it necessitates working at a moderate heat, and thereby rendering the decomposition very slow, and very incomplete if any fused portions are present. It is also impossible to avoid a loss of sulphur in the shape of sulphur dioxide in this operation. The advantage of the process at the time of its introduction lay in the possibility of working up worthless small ore and of obtaining from the residue small quantities of copper and tin, not otherwise recoverable. The saltcake certainly contained too much common salt to be employed directly in alkali-works, and had first to be heated with sulphuric acid in ordinary decomposing-pans. Longmaid conveyed the gas generated in calcining through wooden flues submerged in water, where muriatic acid and ferric chloride condensed, whilst chlorine passed on and was used for making bleaching-powder; of course this was only very weak, and had to be brought up to the proper standard by chlorine obtained in the usual way, which no doubt was found impossible in practice.

Longmaid's process was carried out for a number of years by the inventor himself, at St Helens in Lancashire, at Ardrossan, and at Wallsend-on-Tyne. In Scotland[1] a schist containing pyrites (say 10 to 30 per cent. of sulphur) was ground up with crude rock-salt, moulded into bricks, dried, and calcined in a kiln. After three or four weeks the decomposition was pretty complete. The burnt bricks were lixiviated, the liquor evaporated to dryness, the residue treated with sulphuric acid and heated strongly, in order to decompose ferric and aluminic chloride. A similar material was that remaining at Gouhenans (Haute-Saône), from the preparation of slaty coal for sale.

The process employed at Wallsend for some time was more similar to the original process of Longmaid, and differed from it chiefly in the furnace (sketched in Figs. 52 and 53). The reverberatory furnace, heated by a fireplace, *a*, has only two beds, *b* and *c*, of which *b* is horizontal, *c* rising towards the back; above the back part of *c* rises the kiln *d*, whose grate-bars *e e* are easily movable in the openings *i i*; on the top it is closed by the lid *f*, used for charging. *g* is a flue leading from the kiln; *h* another, leading from the furnace to the chimney; both are provided with dampers. The openings *i i* also serve for admitting and regulating the air; this can also be done from the working doors *k k*. The fresh mixture is first charged through *f* into the kiln *d*; then, when the charge has been withdrawn from *b* and that from *c* has been moved forward on to *b*, the grates *e e* are drawn out and the contents of *d* dropped into *c*. The grates then are put in again, and *d* is charged anew. Usually the fire-gas travels from the interior of the furnace through the kiln *d*, and from this through *g* to the chimney; but if the heat becomes too great, the dampers are so placed that a portion of the fire-gas is conveyed away by *h*.

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[1] *Wagner's Jahresber.*, 1861, p. 171.

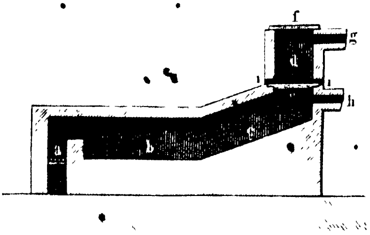

FIG. 52.

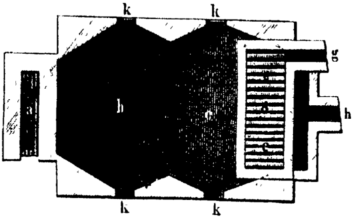

FIG. 53

Longmaid's process has not been able to compete with the usual one, both on account of the above-mentioned incompleteness of the decomposition, which necessitates a treatment with sulphuric acid, and owing to the necessity of lixiviating the product of calcination and consuming fuel for making anhydrous sulphate. It has consequently been given up for some time; but it has given an impulse to two important processes, viz., copper-extraction by calcining with salt, and the preparation of saltcake by roasting the pyrites apart from the salt, and thus doing away with the lixiviation. The last-named process is described in detail in Chapter V.

Weldon, on 5th February 1872, patented the manufacture of saltcake by heating common salt with *manganese sulphide*, along with air, or with air and steam together—also from NaCl along with Mn_2O_3 and CuO or Fe_2O_3 in a current of SO_2 and air, also with steam—or in a current of SO_2, or of CO—in short, a large number of combinations, none of which seems to have found any practical application.

According to a patent taken out by Hutchinson (1st January 1876), a finely powdered mixture of alkaline chlorides and metallic sulphides or brimstone is dropped down in a tower or revolving cylinder, whilst a red-hot mixture of air and steam traverses it; or the chlorides are to be dropped by themselves as a rain, and brought into contact with the gas from burning the metallic sulphides by themselves, mixed with air and steam. This is especially recommended for the gas from metallurgical operations, which is otherwise lost. The first proposal would agree with Longmaid's, the second with Hargreaves's process, with this difference, that the substances are brought into contact with red-hot gas in the shape of a rain of dust. The escaping muriatic acid, mixed with chlorine, is to be utilised in the usual way. This process seems to offer unsurmountable practical difficulties, and will hardly come into operation for the manufacture of saltcake.

For modifications of this idea, reference may be made to the proposals of Basset (Fr. P. 477353, of 1914), and P. B. Heilbronn (Ger. P. 295074, of 1915).

4. *From Common Salt and Magnesium Sulphate.*—Scheele as early as 1787 observed that, if solutions of magnesium sulphate and sodium chloride are mixed and the solution cooled down to at least −3° C., Glauber's salt crystallises out and magnesium chloride remains in the mother-liquor.[1] But probably the "Friedrichsalz," sent out from the Friedrichshall saltworks since 1767, was made in the same way, of course without any understanding of the process. We shall mention later the application of the same reaction to the mother-liquors of the salt-gardens in the south of France, and to the residue from dissolving the potash salts at Stassfurt. As a real principal product, Ramon de Luna[2] proposed to make sodium sulphate from the Epsom salt found in several parts of Spain, especially near Madrid. An intimate mixture of 2 parts of crystallised or 1¼ part of slightly dried Epsom salt and 1 part of common salt is to be brought to a red heat: hydrochloric acid escapes, and the residue consists of a mixture of sodium sulphate and magnesia. If this is treated with water at 90° C., sodium sulphate, with any undecomposed magnesium

[1] Wagner, *Regesten der Sodafabrikation*, p. 25.

[2] *Wagner's Jahresber.*, 1855, p. 59.

sulphate, is dissolved; the latter is converted by milk-of-lime into calcium sulphate and magnesia, and thus removed. De Luna in this way prepared 12 tons of Glauber's salt, but he has had no successor.

Long before him, Lord Dundonald had used the same plan. In his patent of 28th February 1795, he proposes to make Glauber's salt by mixing sea-salt or rock-salt with the sulphate of alumina, iron, or magnesia (expressly mentioned as "Epsom salts"), or with gypsum, all in solution or otherwise, adding to this a suitable quantity of clay, preferably such as contains iron, drying, grinding, and heating in a reverberatory furnace, crucible, or the like, till the muriatic acid is driven off. After this the Glauber's salt is to be extracted by lixiviating and washing, and to be obtained by crystallisation or evaporation to dryness. Epsom salt and rock-salt react to yield the product even without addition of clay containing iron, but not so completely.

Margueritte in 1855 obtained a patent for the *indirect* preparation of sodium sulphate by calcining salt with lead sulphate and regenerating the lead sulphate by treating the lead chloride with magnesium sulphate or calcium sulphate.

The magnesium sulphate process became of practical importance only when an extremely cheap source of that salt had been discovered in the Stassfurt *kieserite*. Kieserite ($MgSO_4$, H_2O) is obtained at Stassfurt from the residue remaining in the treatment of the "Abraumsalz" for potash salts. This residue contains 55 to 60 per cent. of common salt, 25 to 30 per cent. of magnesium sulphate, a little potassium chloride, anhydrite, clay, boracite, and water. The working-up of kieserite for Epsom salt ($MgSO_4$, $7H_2O$) and subsequent preparation of other salts from it, was first proposed by Clemm[1] (French patent of 6th October 1863). Whilst his other proposals have not turned out successful, his process for separating the kieserite itself is employed up to the present time. The residue from dissolving the Abraumsalz is treated with a current of cold water in a tub with a perforated false bottom; the kieserite is thus washed away in the state of flour, the rock-salt being partially dissolved and partially remaining behind in larger pieces. The water, with the particles suspended in it, is separated from the coarser particles by a fine sieve, and then subjected to fractional settling; thus the kieserite is obtained in a comparatively pure state, viz., with 55 to 60 per cent. $MgSO_4$, 8 to 10 per cent. $CaSO_4$, 2 to 4 NaCl, the remainder being H_2O. By exposure to the air and treatment with hot water, Epsom salt can easily be obtained from it, and from this also Glauber's salt by Balard's process. For this purpose, however, since 1865, the crude residue from the dissolution is usually employed, which at the same time contains the necessary common salt. At first great difficulties were met with in making and working up large quantities of liquor in the cold of winter. The employment of ice-making machines seemed too expensive; and even the idea of making from the residues, directly after dissolving the potassium salts, a liquor adapted for obtaining sodium sulphate, and keeping this in water-tight brick tanks till winter, was found difficult to realise, as the tanks could not be kept tight. After sufficient experience had in this way been gained, manufacturers have reverted to making the solutions of Glauber's salt only in winter and during sufficiently frosty weather; the residues obtained during other seasons from dissolving the potash salts, first weathered in heaps, together with those made in winter, are quickly dissolved by steam in vessels provided with agitating machinery, allowed to settle, and exposed to the frost in large wooden coolers. At one works the residues are simply dissolved by tepid water run over them in tubs provided with a perforated false bottom. This process can only be employed for completely weathered residues, and does not yield as much as the former. Such residues, weathered for some years, contain all the kieserite already converted into Epsom salts. An analysis showed:—

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[1] *Wagner's Jahresber.*, 1864, p. 256.

$MgSO_4$	14·49
Na_2SO_4	13·96
$CaSO_4$	2·26
NaCl	27·09
KCl	1·60
Insoluble	10·48
Water	30·12

The fresh residues must be freed from adhering magnesium chloride and carnallite by washing with water, because these greatly interfere with the crystallisation of Glauber's salt, which, however, is much assisted by an excess of common salt (see above); the residues are therefore picked in such a way that they contain 4 mols. of NaCl to 1 of $MgSO_4$.

The crude Glauber's salt obtained in this way has the following average composition:—

Na_2SO_4	40·22
NaCl	1·23
$MgSO_4$	0·47
$MgCl_2$	0·92
$CaSO_4$	1·12
Insoluble	1·40
Water	54·64

It is useless for most purposes, on account of its impurities, and is therefore either dissolved and recrystallised (*refined Glauber's salt*) or converted into calcined sulphate. In both forms the glassworks prefer it to the sulphate made by decomposing common salt with sulphuric acid, as it is quite free from acid and almost completely free from iron. The average composition of the calcined sulphate is:—

	1st quality.	2nd quality.
Na_2SO_4	97	94
$CaSO_4$	1·1	1·1
NaCl	1·6	2·5
Insoluble	0·3	2·2
Fe_2O_3	0·04	0·07

Following this process, the works of the Leopoldshall United Company in the winter 1872-73 made about 3750 tons, in 1873-74 about 7500 tons, in 1874-75 12,500 tons, of crude Glauber's salt.

The coolers have a surface of 12,000 square metres, and in frosty nights furnish up to 150 tons of crude crystals in twenty-four hours. If all the Leopoldshall and Stassfurt works would work up their residue in a similar manner, 35,000 tons of crystals, or 11,500 to 12,000 tons of calcined sulphate, could be obtained; but as this takes much space and capital, and the cost price of the sulphate is hardly less than that made in the usual way, many factories prefer only washing for crude kieserite. (This description is by Dr Frank, in Hofmann's *Ber.*, 1875, p. 363.)

The crystallised Glauber's salt can be obtained either in large crystals similar to soda, or in small ones similar to Epsom salt. This similarity in the appearance of the crystals led to the extensive use of soda and Glauber's salt, for the adulteration of Epsom salt at one time.

In 1887 about 10,000 tons of crystallised Glauber's salt was actually made in Stassfurt, whilst the quantity obtainable from the liquors would be from 50,000 to 70,000 tons per annum.

During recent years the production of Glauber's salt at Stassfurt has remained stationary or has even gone back to some extent, as it does not pay very well. Some factories recently erected have not taken up this branch at all, and others employ the kieserite residues for the manufacture of potassium sulphate.

The above descriptions may be supplemented by another, taken from E. Pfeiffer's *Handbuch der Kali-Industrie*, concerning the style of work pursued at Stassfurt. The raw material is the residue from dissolving carnallite in the manufacture of chloride of potassium. It contains from 45 to 55 per cent. $NaCl$, 25 to 30 per cent. $MgSO_4$, etc.; and with it are worked up some natural mixtures of a similar composition, occurring in certain strata at Stassfurt. When kieserite is cheap, a mixture of this with rock-salt is used as well. The equation requires 97·43 parts of $NaCl$ to 100 parts of $MgCl_2$; in practice twice as much $NaCl$ is employed. The work is greatly facilitated by exposing the residue to the action of the air, at least for a week. The work of dissolving it is the principal item of cost. The best yield is obtained in the following way:—The residue is broken up with pickaxes, or, in case of necessity, blasted, and thus reduced to pieces of the size of a fist, or, at most, of a man's head; it is then put in wooden tubs, holding from 150 to 280 cub. ft., and provided with a false bottom, with holes ⅜ in. wide, covered up with old jute bags. It is there covered with water of 45° or 50° C., which ought to form a solution of sp. gr. 1·27 to 1·29 at 38° C., at which temperature it is run into the coolers. One cub ft. of residue can yield 5 cub. ft. of liquor. This older process is very good, but it involves the breaking up of the residue and moving it twice, which is carried out by the following process, practised in the majority of recent works:—The residue from dissolving the crude carnallite is run quite fresh and warm into dissolvers, placed on a lower level, and is there treated with water and a little steam, with constant mechanical stirring for a quarter or half an hour. This produces a liquor, of sp. gr.

1·32 to 1·345 in the muddy state, which is brought to the proper composition, if needful, by adding some magnesium sulphate or common salt. The clarified solution shows on an average a sp. gr. = 1·28, and contains from 8 to 12 per cent. $MgSO_4$, 16 to 23 NaCl, 1 to 2 KCl, 2 to 3 $MgCl_2$, 65 to 66·5 H_2O; per cubic foot = 6·37 to 9·58 lb. of $MgSO_4$, corresponding to from 17 to 25·6 lb. of Na_2SO_4, $10H_2O$.

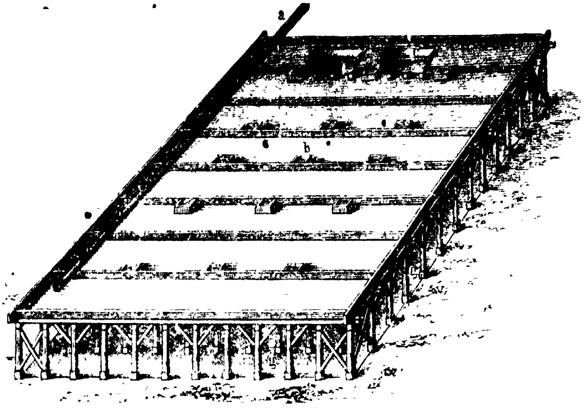

FIG. 54.

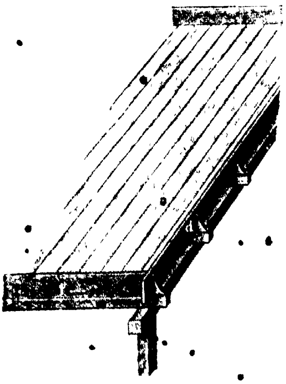

FIG. 55.

The crystallisation of Glauber's salt from these liquors takes place during frosty nights in shallow wooden coolers, as represented in Fig. 54, on a scale of $\frac{1}{400}$; Fig. 55 shows a corner on a scale of $\frac{1}{50}$. These boxes are carried on posts and girders, and are composed of 1½-in. planks, *e*, with joints caulked with hemp and tar-pitch; the sides, *f*, are strengthened by stays, *d*, and leave an available depth of 8½ in. Corresponding to the usual length of the planks, each box is divided into eight compartments, leaving a number of holes, *b*, free for casting out the salt, lying on the eleven wooden drainers, *c*. The fresh liquor is supplied by spout *a*. The space below the cooling-boxes is employed for warehousing purposes. Such a cooler, with pillars, etc., costs £270. One works at Leopoldshall possesses five coolers with a surface of 58,350 sq. ft., which have sometimes yielded a crop of 150 tons in a single cold night. Early in the morning the mother-liquor (of sp. gr. 1·20 to 1·225) is run off before it has had time to get to a higher temperature. At some works they use iron coolers.

The crude Glauber's salt contains from 3 to 9 per cent. of mother-liquor, with 27 per cent. of foreign salts (KCl, NaCl, $MgCl_2$, $MgSO_4$). The purification of the salt will be described in Chapter VI.

Proposals for modifying the Ordinary Process.—Clemm's proposal of 1863, mentioned above, was the following:—To 1 molecule of NaCl 2 equivalents (= 1 molecule) of kieserite is employed, because if an equivalent quantity is used only half of the NaCl is decomposed and a double salt of Na_2SO_4 and $MgSO_4$ is formed. If the double equivalent of kieserite is taken and the mixture boiled sufficiently long with water, all the NaCl can be decomposed. The solution is evaporated to dryness and the residue treated with steam at a red heat: HCl escapes, and the double salt remains behind, mixed with magnesia. These are separated by lixiviation; and on evaporating the solution the sodium sulphate separates in an anhydrous state. These reactions, however, do not go smoothly in practice, and the saltcake thus obtained is too dear.[1]

Townsend (B. P. 1703, of 1879) mixes 50 lb. of magnesium sulphate with 48¾ lb. common salt, dries and heats in a retort, blowing in steam; HCl escapes, while Na_2SO_4 and MgO remain behind. A later patent of the same inventor (Ger. P. 29307) describes modifications of his plan. Sprenger's patent (B. P. 728, of 1881) comes to the same thing. Precht[2] declares all these proposals to be quite unworkable.

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[1] Michels, *Wagner's Jahresber.*, 1865, p. 288.

[2] *Fischer's Jahresber.*, 1881, p. 219.

5. *From Common Salt and Calcium Sulphate.* — Lord Dundonald's proposal for this has been already mentioned. The next proposal of the same kind is stated, in Wagner's *Regesten*, p. 29, to have been made by Hodson; but no such patent appears in the English list, and there may possibly be a confusion with Wilson, who on 22nd November 1838 took out a patent, in which it is prescribed to boil together common salt, gypsum, and magnesium carbonate by steam in certain proportions. Calcium carbonate is formed, and from the solution, on concentration, anhydrous sodium sulphate is separated; magnesium chloride remains in solution. The magnesia is precipitated by lime, and reconverted into carbonate by a current of carbonic acid. Tilghman (patent of 1st February 1847), among many other things, also proposed to bring equal parts of common salt and gypsum to a red heat in fireclay cylinders lined with magnesite, and to conduct superheated steam over the mixture; the escaping muriatic-acid gas is condensed, and the residue worked up by lixiviation. This process has never been carried out on a large scale; and it could not succeed, as Knapp found[1] that the commencement of decomposition could be observed in a glass tube, but not in a gun-barrel—according to which, silica seems to play a part in Tilghman's process.

That on melting together common salt and gypsum no decomposition takes place, has been shown by Trommsdorff,[2] Karsten,[3] and H. L. Buff.[4] Greenshields (B. P., December 1852) states that by adding powdered coal or coke, igniting and lixiviating, not pure sulphate but a product containing much sodium sulphide, is obtained, which was to be worked up with small coal and calcium carbonate in an ordinary black-ash furnace.

Nicklès[5] ignites a mixture of anhydrite, rock-salt, and manganese dioxide. The manganese dioxide interacts with the sodium chloride with liberation of chlorine, whilst sodium sulphate and lime remain behind. In this process, however, at most 15 per cent. of sodium sulphate can be obtained; also, the volatility of sodium chloride at a red heat is inconvenient for this and any similar processes.

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[1] *Liebig's Jahresber.*, 1847-48, p. 1054.

[2] Gmelin-Kraut's *Handbuch der Chemie*, 5th ed., ii., p. 185.

[3] Wagner's *Regesten*, p. 29.

[4] *Dingl. polyt. J.*, clxxii., p. 282.

[5] *Répert de Chim.*, appl. 1862, p. 364.

Anthon[1] obtained an Austrian patent for the following process. It is based on the fact that magnesium carbonate is completely decomposed by calcium sulphate, magnesium sulphate, and calcium carbonate being formed, and on the other fact that common salt and magnesium sulphate yield sodium sulphate and magnesium chloride. Equivalent proportions of common salt, calcium sulphate, and burnt magnesia are mixed with a weight of water from 6 to 8 times that of the common salt; and, with constant agitation, carbonic acid is passed through up to saturation; the solution is separated from the calcium carbonate formed, and evaporated, whereupon Glauber's salt crystallises out, and magnesium chloride remains in the mother-liquor. Or magnesium carbonate is employed from the first, and the mixture stirred for three or four hours. The magnesia is to be obtained by burning magnesite or dolomite, by precipitating magnesium chloride with lime, or by sufficient heating of magnesium chloride.

Another indirect method of preparing sulphate from gypsum was patented in Bavaria by Bandiner in 1832[2]; it has been proposed again by Fleck[3] and Reinsch,[4] and consists in converting finely powdered gypsum by means of ammonium carbonate into ammonium sulphate, and preparing from the latter, by sublimation with common salt, sodium sulphate, and sal-ammoniac.

Vogt and Figge (Ger. P. 34028) mix alkaline chlorides and calcium sulphate with magnesia, and heat these in a cupola from without by gaseous fuel, whilst superheated steam is passed through the mass; HCl escapes, and a mixture of Na_2SO_4, CaO, and MgO remains behind. [This process cannot possibly work in an economical manner.]

From gypsum and alkaline sulphites the Chemische Fabrik Grünau (Ger. P. 48269) proposes to manufacture sodium sulphate by first neutralising the sulphite liquor with lime and then mixing with gypsum; $CaSO_3$ is precipitated and is utilised as well. Such liquors are formed when alkaline sulphonates are melted with caustic soda for manufacturing phenols; also as waste liquors from the manufacture of wood-pulp, etc.

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[1] *Dingl. polyt. J.*, clxxi., p. 138.

[2] *Wagner's Jahresber.*, 1858, p. 102.

[3] *Fabrik. chem. Prod. aus thier. Abfallen*, p. 131.

[4] *Wagner's Jahresber.*, 1870, p. 167.

6. *From Common Salt and Ammonium Sulphate.*—This process, in which sal-ammoniac is the principal object and sodium sulphate only a by-product, has been already mentioned. The process has been employed since 1795 at Grenelle in France, later on by Pfluckner, Persoz, Poole, and others, and is still in common use. One equivalent of ammonium sulphate and two of common salt are dissolved in warm water and evaporated, so that anhydrous sodium sulphate is separated. When the liquid is concentrated up to the point that a drop solidifies on cooling, it is run off; on cooling, sal-ammoniac crystallises out. The proposal of Bandiner, mentioned in No. 5, belongs to this class as well.

7. *From Common Salt and Aluminium Sulphate or Alum.*—This process has been already mentioned, where sodium sulphate is a by-product; as principal product it was made about 1750 by Constantin at Welle, near Osnabruck, from alum,[1] and by Lord Dundonald in 1795 from aluminium sulphate (see p. 168). The same decomposition has been again carried out (according to Wagner's *Regesten*) by Gren, S. Hahnemann, Fuchs, Piepenbrinck, and Tuhten; Pelouze and Kuhlmann's patent of 1850 and Cunningham's patent of 1850 also belong to this class. In this process the object is either the preparation of alumina,

$$Al_2(SO_4)_3 + 6NaCl + 3H_2O = 3Na_2SO_4 + Al_2O_3 + 6HCl,$$

or of aluminium chloride,

$$Al_2(SO_4)_3 + 6NaCl = 3Na_2SO_4 + Al_2Cl_6.$$

Since most alum is nowadays not made from aluminous schist, but from sulphuric acid and clay, such a preparation of sodium sulphate can no longer take place as a principal product, but only as a by-product in making aluminium chloride for dyers, etc.

8. *From Common Salt and Ferrous Sulphate or Other Iron Salts.*—That sodium sulphate can be obtained from ferrous sulphate and common salt, either by igniting them together or by mixing the solutions of both salts and exposing to the cold of winter, has long been known. The former process was

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[1] Wagner's *Regesten*, p. 33.

described in 1789 by S. Hahnemann, the latter by H. van der Ballen, Lieblein, Tuhten, and Wiegleb[1]; Lord Dundonald, in 1795, likewise mentions it. As early as 1793, Athenas had an alkali-works in Paris founded upon it. Wilson, on 22nd November 1838, patented the addition of common salt to a boiling solution of ferrous sulphate, whereupon anhydrous sodium sulphate is precipitated and washed with a hot saturated solution of common salt, in order to remove the mother-liquor of ferrous chloride. He further converted the latter into ferrous hydrate, and by means of this prepared sodium hydrate.

According to Berzelius,[2] at Fahlun sodium sulphate was obtained from the pit-water and from the mother-liquor obtained in making copperas, by mixing them with the proper quantity of common salt, evaporating to dryness, and igniting. The pit-water contains several sulphates, especially those of iron, which on igniting decompose the sodium chloride to form sulphate, whilst metallic chlorides are formed and partially volatilised; partially they give up chlorine and take up oxygen from the air. The calcined salts are dissolved in boiling water, and a crop of sodium sulphate crystals is obtained on cooling. Abich introduced the same process at Schoningen, and employed the ferrous chloride remaining in solution for making Prussian blue.[3] But in 1819 the same thing exactly was described in a patent of Fuller's. In spite of all this the process was described as new in 1852 by E. Thomas, Delesse, and Boucard.[4]

Macfarlane[5] ignites dried copperas and common salt in a current of air. At first ferric chloride is formed; and this yields ferric oxide and chlorine; so that the residue contains sodium sulphate and ferric oxide. An addition of ferric oxide assists the reaction by making the mass more porous and less fusible. Eight hundred and twenty-eight parts of copperas are dried in a gentle heat and partly oxidised, intimately mixed with 352 parts of sea-salt and 78 parts of ferric oxide, brought to a low red heat in a muffle-furnace, and a current of air dried by caustic lime is conducted over the mixture. The temperature should not be so high that ferric chloride can sublime: the mass must be stirred from time to time. In this case only chlorine escapes, mixed with nitrogen:

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[1] Wagner's *Regesten*, p. 30.

[2] *Lehrbuch der Chemie*, 4th ed., iv., p. 153.

[3] Mitscherlich, *Lehrbuch der Chemie*, 1847, ii., p. 58.

[4] Wagner, *loc. cit.*

[5] *Silliman's Journal* [2], xxxvi., p. 269.

$$2FeSO_4 + 4NaCl + 3O = 2Na_2SO_4 + Fe_2O_3 + 2Cl_2.$$

In the muffle there remains a mixture of ferric oxide and sodium sulphate, which is, without lixiviation, converted into caustic soda and iron sulphide by a process to be described in the Third Volume. Even this process, where lixiviation is avoided, does not pay.

Persoz and Kuhlman[1] in 1850 obtained a patent for decomposing common salt by alum-mud, basic ferric sulphate, or calcined alum-schist—that is to say, essentially the same materials as the last, only already partially oxidised. They also introduced steam during the heating, so that the reaction will be

$$Fe_2(SO_4)_3 + 6NaCl + 3H_2O = 3Na_2SO_4 + Fe_2O_3 + 6HCl.$$

The residue is to be separated by lixiviation.

It is evident that the process employing ferrous or ferric sulphate in the dry way is a transition to calcining pyrites with common salt (usually called Longmaid's process, *supra*, p. 163); the latter is however preferable, because the ferrous sulphate is not separated, but employed at once in the nascent state.

9. *Common Salt and Cupric Sulphate* (Wilson, 1838; Hunt 21st January 1840).

10. *Common Salt and Zinc Sulphate* (Hunt, 1840; Boulton, B. P., 23rd February 1852; Kessler[2]).—In both cases the process is essentially the same as that of Wilson, described above for ferrous sulphate; only the mother-liquors of cupric or zinc chloride are precipitated by lime, and the oxides worked up in various ways. Here the manufacture of sodium sulphate as principal product is out of the question. To this class belong the manufacture of sodium sulphate from the mother-liquors of the wet copper-extraction.

11. *From Common Salt and Manganese Sulphate.*—Barrow (B. P., 26th February 1856) describes this process, which is quite analogous to the former ones, as part of a very unpractical and complicated new process for manufacturing alkali.

12. *From Common Salt and Lead Sulphate.*—Margueritte in

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[1] *Dingl. polyt. J.*, cxxxiv., p. 394.

[2] *Wagner's Jahresber.*, 1859, p. 244.

1855 patented the following process:—Equivalent proportions of lead sulphate (obtained by calcining galena) and common salt are mixed, and the mixture is heated for a long time in retorts or open roasters up to a bright red heat. Sodium sulphate and lead chloride are formed; the latter is volatilised, and condensed in a suitable apparatus. The residue contains undecomposed lead sulphate and sodium sulphate, which are separated by dissolving and evaporating; the lead chloride is again converted into sulphate by means of gypsum or Epsom salt, and it is therefore the latter that furnishes the sulphuric acid, not the lead sulphate, which only serves as carrier. The reactions are:—

$$
\begin{array}{lll}
\text{I.} & 2NaCl + PbSO_4 = Na_2SO_4 + PbCl_2; & \\
\text{II.} & PbCl_2 + MgSO_4 = PbSO_4 + MgCl_2 & \\
 & \quad (\text{or } CaSO_4) \qquad\quad (\text{or } CaCl_2) &
\end{array}
$$

This process was described in detail[1]; it has never bee carried out on an industrial scale, in which a complete cor densation of lead chloride and the avoidance of other losses of lead could certainly not be expected.

13. *From Manganese Hyposulphate (Dithionate).*—This salt is obtained by digesting manganese peroxide with an aqueous solution of SO_2. Condy (B. P. 5383, of 1885) prescribes treating manganous dithionate with aqueous solutions of nitrates, chlorides, or acetates, whereby nearly all the alkali is converted into hyposulphate, which is not very soluble in the solution of manganous salts. The dithionate is converted into very pure sulphate by igniting. This is evidently intended to be used in connection with the manufacture of permanganate.

14. *From Sodium Silicate.*—Basset (Fr. P. 386682, of 1908) proposes two methods of manufacturing sodium sulphate from sodium silicate: (1) By fusing a mixture of sodium silicate and calcium sulphate and lixiviating the product; or (2) by mixing calcium sulphate with a solution of sodium silicate and dissolving out the sodium sulphate formed. Sodium silicate must be obtainable more cheaply than at present before either method is like to be used commercially.

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[1] *Dingl. polyt. J.*, clviii., p. 208.

B. *Sulphate of Soda obtained as a By-product.*

In most natural waters we find small quantities of sodium sulphate, or, to speak more correctly, of sulphates and sodium salts at the same time. Preparation of Glauber's salt from this source on an industrial scale is only exceptionally possible, chiefly when the liquid has been previously concentrated for other purposes, and Glauber's salt can be got from the mother-liquors. This is especially the case in the manufacture of common salt from sea-water or from brine; Glauber's salt can be made both from the mother-liquors and the pan-scale obtained in this manufacture.

Sodium sulphate, usually in a very impure state, is manufactured as a by-product in sundry chemical manufactures.

I. *In manufacturing hydrochloric acid* from common salt and sulphuric acid, in cast-iron cylinders and in glass retorts (Chapter III., *supra*, pp. 73 *et seq.*). Here hydrochloric acid is the principal product; and in manufacturing it less than the theoretical quantity of sulphuric acid is employed, both because common salt is much cheaper than sulphuric acid and may rather be in excess, and because contamination of the distilling hydrochloric acid by sulphuric acid is thus avoided. This manufacture is still carried on in several places on the Continent and in the suburbs of London, but on a small scale nowadays. The product is called *cylinder-cake* or *saltcake*, the latter in the north-east of England, whilst this expression in the west always meant ordinary calcined sulphate: it contains from 7 to 10 per cent. of NaCl in excess; and its use is restricted to glass-making and to a few alkali-works, where it is mixed with a little more sulphuric acid in the ordinary saltcake-furnaces and made into finished sulphate. It is, however, very difficult to sell. This process is discussed in detail in Chapter III.

II. *Manufacture of Saltcake and Hydrochloric Acid from Nitre-cake.*—In the manufacture of nitric acid, the proportion of sulphuric acid to sodium nitrate is usually such as to yield a product which approximates more closely to acid sodium sulphate than to the neutral sulphate. Calculated from the acidity, the product "nitre-cake" usually contains about 30 per cent. of "free acid," but varies between wide limits (7 to 35 per cent.) in various works. Large quantities of nitre-cake were used up in the Leblanc-soda works, by mixing it with a quantity of salt corresponding to the amount of "free acid," and adding this mixture to that normally charged to the saltcake pans. This is by far the most rational process when a Leblanc-soda factory is near by, but nitre-cake is often produced in places remote from soda works. Where there is a market for neutral sulphate, *e.g.*, for glass-making, or where hydrochloric acid is required, nitre-cake can often be utilised by one of the processes given below. Nitre-cake is not readily saleable, and the saltcake manufacturers do not pay much for it so that if there is any local demand for hydrochloric acid, saltcake, or Glauber's salt, it may be well worth while to manufacture from the almost valueless nitre-cake even on a comparatively small scale. A special advantage of certain furnaces, such as that of Six and Guttmann, is that a very concentrated hydrochloric acid is readily obtained.

Where it is possible to sell crystallised Glauber's salt, this is sometimes made by dissolving nitre-cake in leaden vessels by the help of steam, preferably with addition of some fresh saltcake, settling the liquor and running it into shallow lead-lined coolers, with strips of lead hanging down from the top. The "free acid" remains in the mother-liquor, which is rarely worth anything principally owing to its great percentage of iron.

Herberts (Ger. P. 28769) uses nitre-cake for making Glauber's salt and carbonic acid. He dissolves it, runs it into a lead-lined horizontal cylinder, provided with agitating gear, and adds ground carbonate of lime. The CO_2 is employed at will; the residue in the cylinder is separated by filtration into solid gypsum and a solution of sodium sulphate, which is concentrated by evaporation.

Rommenhöller and Luhmann (Ger. P. 63189) mix nitre-cake with coke-dust, ignite it in a muffle-furnace, and employ the neutral sulphate formed in this way as such, or convert it into sulphide and decompose this by CO_2. The Lothian Chemical Company in 1916 carried out some experiments on the use of nitre-cake in somewhat similar manner. They found that nitre-cake, when warmed with about 5 per cent. of combustible material, such as coal-dust or pitch, decomposed at a very low the sulphur dioxide corresponding to the "free acid." This was never applied on the technical scale but might prove useful, particularly where it could be arranged to utilise the large quantity of sulphur dioxide evolved.

Barbier (B. P. 10450, of 1892) recovers Glauber's salt from a solution of nitre-cake by cooling. A solution of 1·4 or 1·5 sp. gr. on cooling down to 10° yields a crop of crystals of Na_2SO_4, $10H_2O$, whilst sulphuric acid of sp. gr. 1·34 to 1·45 remains in solution, of course together with some unchanged bisulphate, which he proposes to recover by adding 35 or 40 per cent. sulphuric acid of sp gr. 1·80, or better, by evaporating to sp. gr. 1·53. His apparatus consists of a cast-iron or leaden cooler with partition walls, each compartment of which can be cooled at will. For treating 5 tons of nitre-cake per day he requires four compartments of 7 cbm. each, or eight of half the size.

Bouchard-Praceig (Fr. P. 221245) proposes employing nitre-cake for decomposing solutions of bleaching-powder, and makes a calculation, according to which the calcium sulphate ("pearl-hardening") formed pays all expenses, so that the chlorine is got for nothing!

Bollo (B. P. 6898, of 1904) describes precisely the same process, merely adding the employment of mechanical stirring-apparatus.

Chatfield (B. P. 19530, of 1893) dissolves nitre-cake in water, neutralises with ammonia vapour from gas-liquor, etc., and filters. If the nitre-cake had been real $NaHSO_4$ [which is very far from being the actual fact], the solution will contain 48 per cent. ammonium sulphate. Many modifications of this idea were tried and some put into use on a large scale during the war when nitre-cake was plentiful and sulphuric acid difficult to obtain. This and other uses for nitre-cake are dealt with in the volume on Nitric Acid and Nitrates.

Hart (U.S. P. 698704) and the General Chemical Company (B. P. 9875, of 1902) introduce a mixture of common salt and sodium bisulphate (or sulphuric acid) by means of steam in a continuous manner into a revolving cylinder, heated just below a red heat. The HCl escapes continuously, and the sulphate formed, as the inventor asserts, contains neither free sulphuric acid nor sodium chloride.

Hipp (U.S. P. 726533, of 1903) dissolves the nitre-cake, precipitates arsenic, selenium, lead, etc., by means of alkaline sulphides, evaporates the clarified solution down to sp. gr. 1·85, mixes with common salt, and ignites the mixture.

Parker (B. P. 24639, of 1903) dissolves the nitre-cake, neutralises the solution with iron, and treats the solution with sodium carbonate or hydrate.

Hartmann and Benker, (B. P. 1844, of 1907) mix with the ground nitre-cake a large quantity of finely ground ordinary saltcake, fine sand, etc., so that the mass on heating does not flux. When heated to a red heat, free sulphuric acid distils off and ordinary sulphate of soda remains behind.

With the similar claim that formation of a pasty mass at any stage of the process is prevented, J. H. Neild (U.S. P. 1102539, of 1914) proposes the addition of a substantially inert material such as an equal weight of saltcake.

Nibelius (U.S. P. 873070) treats a solution of nitre-cake with "a volatile solvent which dissolves the acid, but in which the sodium sulphate is insoluble." The solution containing the free sulphuric acid is separated from the undissolved normal sodium sulphate, and is subjected to distillation at reduced pressure, in order to recover the solvent in the distillate and the sulphuric acid in the residue. Such solvents are alcohol, wood-spirit, fusel oil, etc.

Garroway (B. P. 11986, of 1905) mixes a solution of nitre-cake with sodium sulphite, prepared from sodium carbonate and SO_2, with the assistance of steam. The SO_2 hereby liberated is absorbed by water.

The Chemische Fabrik Grünau (B. P. 6898, of 1904) prepares normal sulphate and sulphur dioxide from nitre-cake by heating this in a cast-iron retort, provided with a stirring arrangement, together with 12 per cent. sawdust, and 2 per cent. coke-dust (*cf.* the previous patent of Rommenhöller and Lohmann).

E. Teisler (Ger. P. 300723 of 1916) patents the addition of solid substances resistant to hydrochloric acid, such as carbon, in order to prevent segregation of the mixture due to the fusing of the nitre-cake.

A very interesting process has been worked out by Th. Meyer, whose patents have been partially taken out by the firm of K. Oehler, by whom they have been carried out in practice

(B. P. 2856, of 1902; U.S. P. 702877; Ger. P. 186398). Meyer[1] has given a special report on it. An intimate mixture of nitre-cake and common salt is brought up to the requisite (comparatively low) temperature in ordinary muffle-furnaces, no mechanical stirrers being required if the nitre-cake does not contain more than 3 per cent. of moisture. If, therefore, it cannot be used

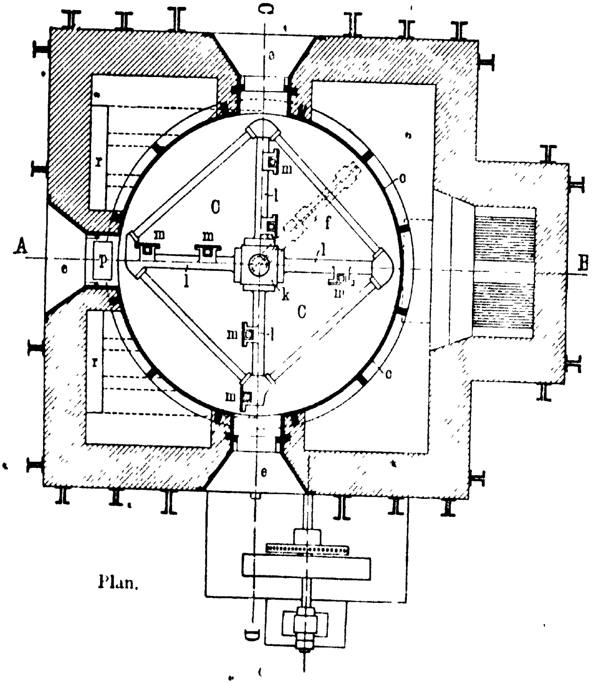

Fig. 56.

while still hot, it should be cooled down in closed boxes, ground in a disintegrator and mixed in slowly revolving cylinders with such a quantity of salt that 1·08 to 2·5 per cent. acid remains in the free (bisulphate) stage. Each furnace receives 10 cwt. of this mixture, and three charges can be turned out in twenty-four hours, yielding each 6 cwt. of sulphate and 5 cwt. of muriatic acid of very high strength. The mass is not fluxed, but merely sintered; a little dry sulphate, previously spread over the furnace bottom, prevents it from acting upon the brickwork. If the muriatic acid is to be entirely free from nitrous acid and chlorine, this is brought about by adding from 2 to 5 per cent. charcoal to the mixture; this generates some SO_2, which destroys those impurities, and at that low temperature no sodium sulphide is

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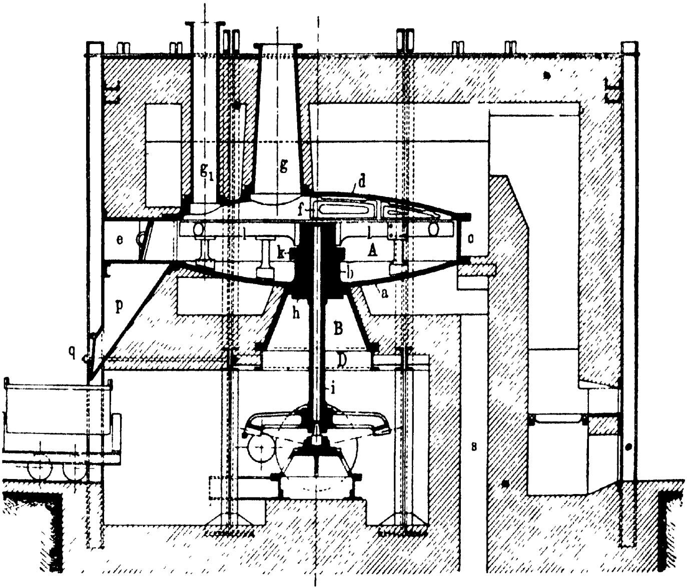
[1] *Chem. Zeit.*, 1906, pp. 1295 *et seq.*

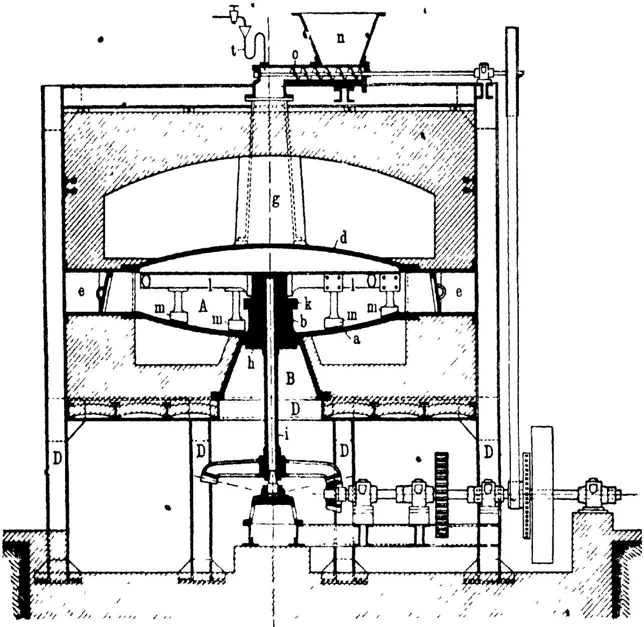


Section A-B.

FIG. 57.

formed. The temperature at the top of the mass should not exceed 450° to 500° as controlled by a pyrometer. Another patent of Oehler's (Ger. P. 165099) describes some improvements in the way of preventing escapes of HCl into the outer air. These processes were in work at Oehler's factory, but were stopped after some time.

Mechanical Furnace.—A process of the Verein Chemischer Fabriken at Mannheim has been working for some years past, and has been found very efficient. A mechanical saltcake-furnace (Ger. P. 137906; B. P. 16207, of 1902) is used. This might serve also for the manufacture of saltcake from common salt and sulphuric acid, but is actually only at work for working-up nitre-cake. The furnace is shown in Figs. 56 to 58. The muffle and stirring apparatus are connected in such manner that no shifting of the machinery can take place. The brickwork serves merely for the fire-flues and for preventing losses of heat. A is the muffle with the pan *a*, the bearing *b*, the cylindrical mantle *c*, and the cover *d*. It rests on the cast-iron frame D. *c e* are cleaning-holes, *f* is a scraper for the cover *d*; *g* the charging pipe, and *g′* the gas-exit pipe. B serves for connecting A with D; *h* a stuffing-box for the revolving shaft of the stirring-machinery C, with the shaft *i*, the nave *k*, the arms *l*, and the scrapers *m*. The mixture is poured into funnel *n*, and



Section C-D.

FIG. 58.

by means of the worm *o* it is charged through *g* into the muffle. The finished product runs continuously through the outlet *p*, with an automatic closing-arrangement, *q*, into trucks. The gases are drawn away through *g*. The fire-gases pass first over the cover and round the mantle, then through the openings *r* underneath the pan, and through *s* into the chimney. This furnace works at a comparatively low temperature, requires but little fuel, and yields very strong hydrochloric acid. One such furnace requires 7 h.-p. and turns out in twenty-four hours 7 tons of saltcake, with 0·5 per cent. NaCl and 1 to 1·5 per cent. free acid; it requires 2 cwt. coal for a ton of saltcake. The pan and cover last about two years, and turn out from 4000 to 5000 tons saltcake; the scrapers must, of course, be renewed more frequently, but the other parts of the machinery last much longer.

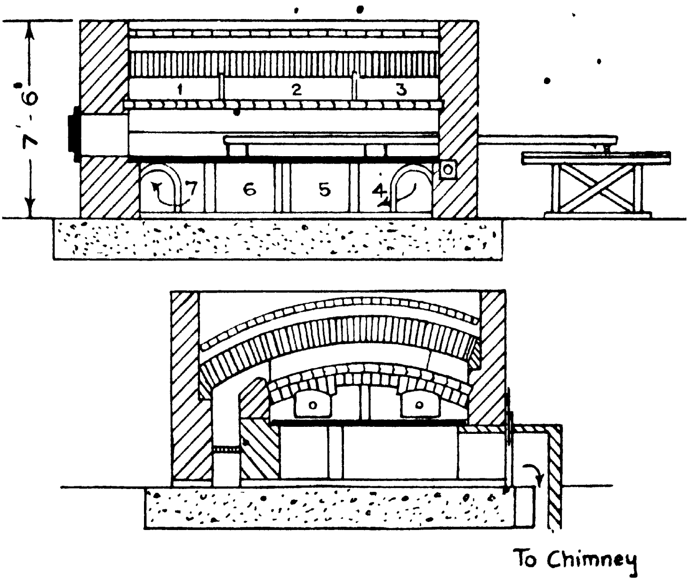


FIG. 59.

Note.—The path of the furnace gases is indicated by numbering the compartments of the muffle and those under the hearth consecutively.

Another Mechanical Furnace.—A furnace operating on the same principle but of different design is that of Six and Guttmann (B. P. 4226, of 1915). The furnace is of the closed or muffle type and is continuous in operation. The bed consists of cast-iron plates on which the mixture is continuously rabbled by rakes attached to two stout iron rods which are moved mechanically to and fro. The general design of the furnace will be seen from Figs. 59 and 60. The furnace can be used for saltcake manufacture in the ordinary manner, or for working up nitre-cake with salt without addition of sulphuric acid. The ground mixture of nitre-cake and salt may be charged either continuously or intermittently

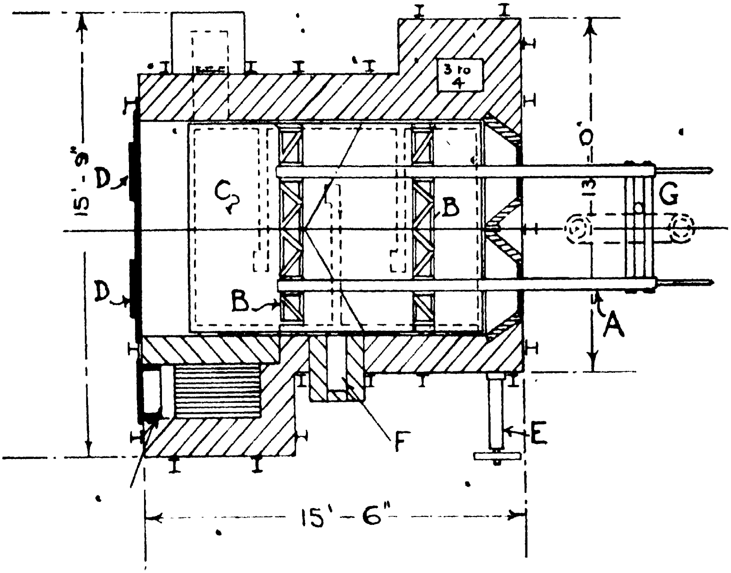


FIG. 60. 5-TON MECHANICAL SALTCAKE FURNACE, TYPE B. (B. P. 4226, of 1915.)
Approximate Scale ⅛ in. = 1 ft.

A. Mechanical Rabbling Arrangement.
B. Rabbles of high speed Tool Steel. Two sets each of two rows of Scrapers.
C. Cast Iron Plates forming Hearth.
D. Special Charging Doors for Salt and Nitre-cake Mixture.
E. Screw Conveyor for removing Saltcake.
F. Hydrochloric Acid Gas Outlet.
G. Mechanism—1½ to 3 H.P. required.

The following figures, based on 1917 costs, are supplied by the patentees for two furnaces of their A type, capable of producing 6 to 10 tons per twenty-four hours:—

Materials—			£	S.	D.
Crushing 1 ton nitre-cake			0	1	0
Salt 7½ cwt. at £2 per ton			0	15	0
Coal, maximum of 3 to 4 cwts. at £2 per ton, say			0	8	0
Total cost of materials			1	4	0
Operation—	S.	D.			
Power, 16 H.P. at 1⅓d. per unit	2	0			
Process wages	5	0			
General wages	1	0			
Repairs, cost of materials	1	6			
Repairs, wages	0	9			
General expenses, light, water, etc.	2	0			
Depreciation, 15 per cent. on £4000	2	0			
Total cost of operation			0	14	3
Total cost of manufacture per ton of nitre-cake			£1	18	3

The above quantity of nitre-cake and salt should yield 1 ton 2 cwt. of saltcake and 11 cwt. of 35 per cent. hydrochloric acid.

Through the courtesy of Messrs The Stavely Coal and Iron Company, Limited, I had the opportunity of inspecting a furnace of this type, and Mr J. A. Wilson kindly gave me some information regarding their procedure. Their nitre cake contains 28 to 32 per cent. of "free acid," and is ground up with the appropriate amount of salt in a pan mill. Charging is done intermittently by means of a long 3-in. steel tube, the part which is thrust into the furnace having the top half removed so as to make a shallow, semi-cylindrical, long tray. This is filled with the mixture, pushed into the furnace along a recess in the centre of the roof, inverted, and the empty tube then withdrawn. The two main rods carrying the rakes are prolonged and pass through bearings at the opposite end to the driving mechanism. This obviates any tendency to droop through support at one end only. At each end of the furnace is a bin, about 12 in. wide and almost the full width of the furnace. The saltcake is raked into these bins by the operation of the rakes, and is withdrawn through doors at the side from time to time. The centre is slightly higher than the end and is the hottest part of the furnace, the temperature at the arch being 600° to

700°. The heating is by means of gas and is consequently readily controlled. Two men per shift were employed, the output being at the time of my visit about 5 tons of saltcake and 550 gallons of 28° to 30° Tw. hydrochloric acid; but this is much below the maximum output of the furnace, being all they required at the time. Hydrochloric acid of 35 per cent. can be obtained, and the condensation and draught arrangements appear excellent. The condensing system consists of (*a*) a catch-tower (*b*) 64 condensers (*c*) a coke-tower, and finally (*d*) a coke-filter.

The catch-tower is in two compartments communicating at the bottom. The first is filled with broken firebrick and the second with Guttmann cells, which are sprayed with the hydrochloric acid returned from the first two condensers. At first the first compartment was sprayed intermittently with the liquid, but the earthenware cracked so frequently that the spraying was abandoned. The acid in the first two condensers is impure and is therefore run back entirely to the catch-tower. The catch-tower is washed out weekly. The condensers, on account of the fact that they were worked much below capacity, required no cooling. After the condensers the gas passes to a tower 30 ft. high and 4 ft. square, inside measurement. The bottom third is filled with Guttmann cells and the upper two-thirds with best Durham coke, graded from bottom upwards. Before passing to the chimney flue, the gas is passed through a small coke scrubber to wash out any uncondensed acid.

Neutralisation of Nitre-Cake.—It would seem highly improbable that saltcake should be made by neutralising nitre-cake, but J. D. Pennock, Solvay Process Company (U.S. P. 870746, of 1907), proposes that alkaline sodium compound be ground with the nitre-cake in approximately reacting proportions and the mixture heated to a temperature above 125°.

During the abnormal conditions prevailing since the war, it has actually paid to carry out a process on these lines, and the author has seen the manufacture of saltcake from nitre-cake by neutralisation in operation. The nitre-cake was fused in an iron pan to drive out water, and the molten mass run slowly into a pan mill in which it was ground up with the requisite amount of dry soda-ash. It was not found possible under any conditions to grind the nitre-cake and soda-ash together without this preliminary heating and fusion. The process gave a poor product and was very uneconomical. Unless left noticeably acid it was dark brown in colour, and it was usual for lumps of nitre-cake to escape neutralisation altogether.

Other Sources of Sulphate of Soda as a By-Product.

In treating *pyrites-cinders* by roasting with salt for the *extraction of copper*, large quantities of sodium sulphate are produced, and many attempts have been made to utilise it, but none of these have been economically successful. Details in volume on Sulphuric Acid.

It has been attempted to make sodium sulphate from *non-cupreous pyrites-cinders*, especially those containing zinc, by special methods; but the economic success is equally doubtful. According to a German patent of the Konigshütte Mining and Smelting Works (No. 28465), roasting with salt has been tried for this purpose.

Urquhart and Rowell (B. Ps. 292 and 293, of 1883) produce sulphate of soda as a by-product in decomposing *sulphate of strontia* with carbonate of soda.

Smaller quantities of sulphate are obtained, for instance:—In the manufacture of *sal-ammoniac* by subliming ammonium sulphate with common salt; in that of *corrosive sublimate* from mercuric sulphate and common salt; in *amalgamating silver-ores*; in making *aluminium chloride* from common salt and alum; in *purifying mineral oils* by mixing the sulphuric acid and caustic lye used in purifying, and skimming off the tar (described by Breitenlohner[1]); in neutralising *organic sulpho-acids* containing a large excess of sulphuric acid by soda; and especially from the alkaline fusion in the manufacture of resorcin, alizarin, etc. Kessler[2] proposes to obtain sodium sulphate from the zinc sulphate of galvanic cells by means of common salt.

In most of the cases just mentioned the sulphate, owing to its low price, cannot be recovered economically, unless at least the crystallised salt is obtained by spontaneous crystallisation without any expense of evaporation. Usually the solutions containing the sulphate are run to waste, because they cannot be profitably worked up.

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[1] *Dingl. polyt. J.*, clxxv., p. 459.

[2] *Wagner's Jahresber.*, 1859, p. 244.

Manufacture of Sulphate from Mother-Liquors and By-Products of Saltworks and Salt-Gardens.

(1) *From Mother-Liquors.* — In these there are always chlorides and sulphates of sodium, magnesium, etc., present (calcium chloride has at a previous stage been converted into gypsum, which has got into the pan-scale), and, according to the temperature, the acids and bases combine in different ways. In the salt-gardens (*marais salants*) on the Mediterranean, worked according to the process of Balard, Merle, and Péchiney (much the same as a process introduced into the Schoenebeck saltworks by Hermann at the beginning of the present century), concentration by spontaneous evaporation, after the purer common salt has been separated, is allowed to go on till (at 58° to 64° Tw.) a crystalline deposit of equal parts of Epsom salt and common salt (*sels mixtes*) has been formed. This is drained, in order to remove, as much as possible, the deliquescent magnesium chloride, dissolved in water up to the point of saturation (55° to 57° Tw.). The solution is cooled in winter by natural cold, in summer by Carré's freezing-machines. Glauber's salt crystallises out, and magnesium chloride remains in the mother-liquor, thus:—

$$MgSO_4 + 2NaCl = Na_2SO_4 + MgCl_2.$$

The decomposition is most complete if to 1 molecule of Epsom salt there are 3 instead of 2 molecules of common salt; then, on cooling to −1° or −2° C., almost four-fifths of all the sulphate which the mixed salts can furnish is actually obtained. It is drained in the cold; and from the mother-liquors at +5° to +6° C. (in autumn) crops of Epsom salt are obtained, which, dissolved with common salt and cooled, furnish new quantities of Glauber's salt. Too much cooling must be avoided, as otherwise carnallite ($MgCl_2$, $2KCl$, $6H_2O$) crystallises out, which ought to happen only with the last mother-liquors. The crude Glauber's salt is sometimes purified by dissolving in tepid water and crystallising.

The sulphate prepared in this way could not possibly compete with that of the alkali-works, unless the common salt and the potassium chloride, which are the principal products, paid the expense of the process, and unless the dehydration of the Glauber's salts was effected in some cheap way, *e.g.*, by Péchiney's process with common salt or *sels mixtes*.

Lunge found the process to be carried on in the following manner at Péchiney's Giraud works:—The *sels mixtes* are corrected by adding magnesium sulphate or common salt, in order to obtain the correct proportions. The mixture is dissolved to sp. gr. 1·263, the liquor obtained later on in dehydrating the Glauber's salt is added, and the whole cooled down to +6° by means of a freezing-machine. The liquefied ammonia is passed through a box, about 13 ft. long, by means of a number of parallel, thin iron tubes, where it is mostly converted into gas; the liquid and gas pass first through another similar box, and then through a solution of "mixed salts," which thereby receives a preliminary cooling, and then returns to an apparatus, where it is converted into liquor ammoniæ by injection of water. The cooled salt solution is conveyed through the freezing-boxes in the opposite direction. The decomposition of the salts into magnesium chloride and Glauber's salt (which separate in small, mud-like crystals) takes place principally in the first box. In this a frame moves backwards and forwards in a horizontal direction, carrying a large number of rakes reaching down between the cold ammonia-tubes. The lower part of each rake moves in a joint which allows a motion only in one direction. When the frame moves towards one of the ends of the box, the rakes drag along and have no effect; when the frame takes the opposite direction, the rakes stand up and thrust the muddy deposit of Glauber's salt towards the other end of the box, where it is lifted up by a chain of buckets and is drained in a trough, lined with thick planks, to prevent cooling. The salt is further drained, still in the cold state, in a centrifugal machine, and is then submitted to Péchiney's dehydration process. Since the dehydration of Glauber's salt by fire is a very awkward operation, whether the fire acts from below or from above, Péchiney utilises the greater attraction for water possessed by the above "mixed salts" at a temperature of 80°. Glauber's salt changes into anhydrous sodium sulphate far below this temperature. The Glauber's salt is mixed with 45 per cent. of its weight of the "mixed salts," the whole is heated to 80°, and is "whizzed" in a centrifugal machine, in which the anhydrous Na_2SO_4 remains behind. The temperature of the magma must never sink below 33°; it is washed with warm water, which leaves Na_2SO_4 with only 4 per cent. water, and almost free from magnesium salt. The solution of "mixed salts" hereby formed is now cooled, in order to separate them as above stated, so that the whole operation costs next to nothing. A dissolving-cylinder of 6½ ft. diameter and 4 ft. high, and a small centrifugal machine form the whole apparatus for dehydrating 13 tons of sodium sulphate.

In hot, dry countries the Glauber's salts can be dehydrated by efflorescence on exposure to the air for a prolonged period. The residue consists of a powder, mainly composed of Na_2SO_4, H_2O, from which the last of the water is easily expelled in a reverberatory furnace; even without this it is directly fit for carriage to a distance and for many applications of saltcake.

(2) *From the pan-scale of salt-works*, which principally consists of the sulphates of sodium and calcium. This is lixiviated with water; gypsum, being insoluble in a solution of sodium sulphate, remains behind. On the large scale, four tanks are ranged side by side, and charged with pan-scale and tepid water. After twenty-four hours the liquid is run off by a plug-hole in the bottom, pumped into the second tank, kept there for another twenty-four hours, and then conveyed into the third, and ultimately into the fourth tank. The first tank has in the meantime been filled with fresh water. This is repeated four times. It is then emptied and the residue of gypsum sold as manure. The liquid from the fourth tank is again brought into contact with fresh pan-scale in the first tank, and thus completely saturated. Liquors of 42° to 44° Tw. are thus obtained in summer and are either kept till winter in wooden tanks, when Glauber's salts crystallises out in frosty weather, or are concentrated by evaporation, filtered through canvas bags, and allowed to crystallise at ordinary temperatures. Long, shallow wooden troughs lined with lead, say 20 ft. long by 6 ft. wide, serve as coolers; the liquid should not stand in them deeper than 3 in., because otherwise too large crystals are formed, which are not liked in the trade. As soon as the crystallisation sets in, a wooden rake is drawn from one end of the cooler to the other; this gentle movement causes the

separation of many individual crystals, which afterwards grow, especially in the longitudinal direction, and thus acquire the peculiar acicular appearance exhibited by the so-called English Glauber's salt. If the liquid were moved too much, or stirred about, as in making Epsom salt, instead of well-formed crystals only a muddy crop would be obtained. If, on the other hand, the liquid is allowed to remain at perfect rest, the salt crystallises principally at the sides and the bottom in the shape of large, firm, well-formed crystals, which must be detached with a chisel and broken up.

When the cooling is complete, the mother-liquor is drawn off by a siphon, the salt is put into a tub with a plug-hole in the bottom, and the liquor drained off clear. The remaining mother-liquor is removed by sprinkling cold water on the salt with a watering-can and allowing it to stand for twenty-four hours to drain. The salt is dried on wickerwork trays, in summer in an open place protected from dust, in winter in a gently heated stove. The crystals are only left in contact with air until they show the first traces of effervescence on their surface; otherwise they would become unsightly in appearance.

(3) *On working-up kelp*, sodium sulphate is also obtained, after the crops of potassium sulphate, potassium chloride, common salt, and sodium carbonate have been got out, just before the working for iodine commences.

(4) *Sodium Sulphate from Cryolite.*—H. Bauer (Ger. P. 52636) shows that on fluxing 5 parts of cryolite with 12 parts of anhydrous calcium sulphate, the following reaction takes place:—

$$Al_2F_6, 6NaF + 3CaSO_4 = 3Na_2SO_4 + 3CaF_2 + Al_2F_6.$$

The melt is boiled with water, the solution is concentrated by evaporation, filtered from the precipitated gypsum, and allowed to crystallise. The same reaction is stated to occur when cryolite and gypsum are boiled with water for a long time. The residual mass of calcium and aluminium fluorides is to be worked for aluminium sulphate and hydrofluoric acid or ammonium fluoride. [It is difficult to understand how an inventor can suppose that a process will pay in which the sodium is turned into almost useless Glauber's salt, and the alumina into a crude residue, whilst in the old process of decomposing cryolite by calcium carbonate the sodium is recovered as carbonate, and the alumina in a pure form.]

CHAPTER V

THE MANUFACTURE OF SULPHATE OF SODA BY THE PROCESS OF HARGREAVES AND ROBINSON

THIS process, which only attained its limited measure of success after years of incessant effort on the part of the inventors, gave promise a few years ago of becoming the chief process for the manufacture of sodium sulphate. Each disappointment only brought forward a new improvement from the inventors until it seemed that the process had fairly established itself.

At the time of its introduction circumstances were in favour of the Hargreaves process, which even in its infancy roused the greatest hopes among the English alkali-makers, and in spite of the great cost of plant, spread with comparative rapidity. In 1891 there were seven Hargreaves plants in Great Britain and Ireland, with 110 cylinders and a producing capacity of 200 tons of saltcake per day; in France three plants, in Germany two plants. Under normal circumstances it is very probable that the Hargreaves process would have extended in an increasing ratio, and perhaps have become the prevailing system of manufacturing saltcake. But it came a little too late. It had hardly got through its earlier stages, when the further extension of the Leblanc alkali process was checked by the ammonia-soda process, with the consequence that the former was compelled to lay the greatest stress on the recovery of the largest possible quantity of highly concentrated hydrochloric acid, which was no easy matter with the Hargreaves process; moreover, Leblanc alkali-makers could not but hesitate to embark further large sums in an industry which seemed to be destined to be extinguished within a comparatively short time.

There are now no Hargreaves plants running in England, the last having closed down in 1918. The fascination of this process for inventors, however, is in itself sufficient to justify a more extended reference than that of most processes mentioned in the last chapter. A full description of the process will be found in the last edition (Vol. II., Part 1, Chap. IV.).

Description of Hargreaves Process.

From time to time, many attempts have been made to manufacture saltcake without the intervention of sulphuric acid, by the direct action of sulphur dioxide, air and steam on sodium chloride. Patents in this direction were taken out, in 1850 by Gossage, in 1853 by Robb, in 1855 by Armbruster and Laist, in 1856 by Rémond, in 1857 by Brooman, in 1858 by Mesdach, in 1863 by Thibierge; also Longmaid's process (1842), itself the revival of a much older process, applied the reaction that comes into play here, in a very different manner from the present. A decisive step was the local separation, first mentioned in Brooman's patent (1857), between the evolution of sulphurous acid from pyrites and its action upon salt. For this reason a patent of Konigs and Henderson (22nd June 1871), which reverts to a mixture of ferric oxide and salt, without any other novelty of importance, has never had any practical success.

None of these former proposals was successful; even the first-mentioned process of Brooman's has never been carried out practically; and the merit of real inventors cannot be denied to Hargreaves and Robinson, whose mutual efforts at length made the process successful.

Hargreaves and Robinson, of course, did not pretend to have been the first inventors of the process of making saltcake by the action of sulphurous acid upon common salt in the presence of air and steam; they only claimed to have made that process practicable by a large number of patents. The first of these dates from 7th January 1870. It gives only an outline of the process; whilst two subsequent patents, of 8th November 1870, already had all the essential features of the apparatus now in use, but with this great difference, that the gas still travelled *upwards* in the cylinders. In their fourth patent, of 4th July 1871, they introduced the following important improvements:—1st, passing the mixed gases in a *downward* direction through the chlorides, by which a more uniform effect is produced; 2nd, employing cast-iron vessels instead of brick chambers; 3rd, combining a series of such vessels in a methodical way, and arranging cast-iron gas-flues, so as to force the gas to act in such a way that the fresh gaseous mixture always comes into contact with nearly finished sulphate, and the almost spent gases with fresh salt, precisely as in the methodical lixiviation of black-ash.

These improvements were of decisive importance. The reason why this process works much more completely if the gases travel *downwards*, has been discussed in a long paper by Hurter.[1]

The most important of Hargreaves and Robinson's improvements was, of course, that of systematically utilising the burner-gas, so that it leaves the apparatus at least as free from sulphurous acid as the gas leaving sulphuric-acid chambers.

Apart from subsequent improvements in detail the most explicit description and drawings of the Hargreaves and Robinson process are contained in their patent of October 1872. Reference may be made also to the paper of John Morrison,[2] and to the last edition of this book in which details are given which are now omitted as being of historical interest only.

General Principles.

When sulphur dioxide in the presence of an excess of oxygen (in the shape of atmospheric air) and of moisture meets with sodium chloride at temperatures round 500°, the following reaction takes place:—

$$2NaCl + SO_2 + O + H_2O = Na_2SO_4 + 2HCl.$$

That is to say: the sodium chloride is converted into sodium sulphate, and the whole of the hydrogen chloride is liberated. This decomposition, in order to be complete, demands a long time and a large excess of the gases and of steam, so that the hydrogen chloride, escaping in the gaseous form, is mixed with very much SO_2, etc. But if these gases are first made to act upon salt already partially converted into sulphate, and later on, when they contain very little SO_2, upon quite fresh common salt, the SO_2 in the gases can be almostly completely exhausted, while at the same time the larger portion of the oxygen and steam are consumed by the reactions described. Thus we obtain at one end of the apparatus sodium sulphate with a little unchanged NaCl and "free acid," *i.e.*, ordinary saltcake; at the other end we find escaping a mixture of HCl with a little oxygen and steam and with very much nitrogen, from which by the ordinary condensers the HCl can be washed out practically completely, and obtained as liquid hydrochloric acid. The reaction is carried out in a set of cylinders which are worked in regular rotation, so that each one is alternately first, intermediate, or last in the series.

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[1] *Dingl. polyt. J.*, **223**, p. 200.

[2] *Transactions of the Newcastle Chemical Society*, **21**, 1881.

The substances used are the following:—The *sodium chloride* is employed partly as pan-salt, partly as rock-salt, but is always moulded in such a shape that it remains permeable to the gases, and can be transformed into sulphate right through. The source of the *sulphur dioxide* is ordinary pyrites-burner gas; of course the gas from sulphur-burners or from roasting blende, etc., would serve the same purpose. In all cases these gases contain not merely a sufficient quantity of free oxygen for oxidising SO_2 into SO_3, but such an excess of that gas as is necessary for making the oxidation practically complete. Experience has shown that the most suitable composition of the gases in the present case entirely agrees with that which is most suitable for the manufacture of sulphuric acid; they should contain not less than 6 per cent. and not more than 8 per cent. SO_2. For this purpose the unavoidable presence of SO_3 in the burner-gas must be counted an advantage.

The way of introducing the *steam* in this process differs very much from that employed at vitriol-works. It is not introduced at some distance from the pyrites-burners, as is the case in lead-chambers, but in the burners themselves, or just behind them. Introduction beneath the grate-bars of the burners was tried but found to interfere with the combustion of the pyrites. It is usual to place the steam-jets within the burner *above* the layer of burning pyrites. The steam is always somewhat superheated. Much less steam is used than in the manufacture of sulphuric acid; it is regulated in such manner that the exit gas contains about 20 grains per cubic foot (46 g. per cubic metre). For every 1000 lb. of Na_2SO_4 theory requires 127 lb. of steam; practically 200 lb. is used.

Morrison quotes the following average composition of the entrance gases from actual practice:—

60 to 70 grains SO_2 per cub. ft. = 138 to 161 grms. per cbm.
2 „ 8 „ SO_3 „ = 4·6 „ 18·4 „ „
20 „ 25 „ H_2O „ = 46 „ 57·5 „ „

It is most important to work at the proper *temperature.* The reaction commences at 400° C., but not very strongly; the cylinders charged with fresh salt, in which the last remainder of SO_2 is to be retained, are kept at that temperature, partly by the heat of the gases passing through and partly by an external fire. At the other end of the series, where the saltcake is finished, the temperature must be much higher, in order to decompose as completely as possible the bisulphate formed by the SO_3 of the burner-gas; that means rather above 500° C. for pan-salt, or 540° for rock-salt. There is no harm done if the temperature rises even a good deal higher than this, so long as the salts do not commence to fuse. Hence 772° C., as the melting-point of NaCl, or even 860° as that of Na_2SO_4, would be the theoretical limit; but it goes without saying that it is imperative to keep considerably below this utmost limit in order to avoid accidents.

The reaction of the Hargreaves' process is strongly exothermic, so that, theoretically, once the substances are brought to the proper temperature, no supply of heat from without is required, but, on the contrary, the heat produced by the reaction must be carried away. In practice so much heat is lost by radiation that external heating is necessary.

In the ordinary saltcake process, the reaction

$$H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl$$

is endothermic, being accompanied by a heat-absorption of 15·8 kilo-calories. In the Hargreaves' process there is, on the other hand, a marked heat-evolution, since the burner-gases enter into the process with their own heat, and the heat of formation of sodium sulphate is superadded to this. The heat developed here is as follows:—

$$\begin{array}{lccc} (1) & 2FeS_2 + 11O & = & Fe_2O_3 + 4SO_2 \\ & 2 \times 23.8 & & 191 + 4 \times 71.6 \text{ heat-units} \\ & 47{\cdot}6 & & 477{\cdot}4 \end{array}$$

That is, for $4SO_2$ 429·8, or for SO_2 107·4 h.u.

$$\begin{array}{lll}
(2) & 2NaCl + H_2O + O_2 + SO_2 = & Na_2SO_4 + 2HCl \\
 & 2 \times 97.3 + 68 + 71.6 & 327.4 + 44 \text{ h.u.} \\
 & 335.2 & 371.4 \quad ,, \\
 & \text{leaving again a surplus of} \quad . \quad . & 36.2 \quad ,,
\end{array}$$

or together with the former 107·4 giving a total of 143·6 h.u.

As the sodium sulphate formed has a specific molecular heat of 36·1, its temperature would theoretically rise to $\frac{143,600}{36 \cdot 1}$, or nearly to 4000° C.: but this calculation ignores the loss of heat with the discharged saltcake and escaping gases and the great loss of heat by radiation. This explains why an addition of heat from without is certainly necessary in the beginning, in order to reach the temperature where the reaction sets in, but that later on, with very good arrangements for preventing loss by radiation, not only is there no necessity for further heating from without, but it may even become necessary to cool the mass artificially, to prevent its fusing.

A detailed and interesting study on the Hargreaves process has been made by W. Staedel.[1] He does not consider it probable that the reaction:

$$4NaCl + 2SO_2 + O_2 + 2H_2O = 2Na_2SO_4 + HCl$$

(in which 9 molecules are supposed to act on the left side) should take place without intermediate reactions. In the first place he studied the influence of temperature and of the concentrations on the reaction by allowing a suitable mixture of gases to act upon small pieces of rock-salt in a glass tube at as uniform a concentration of SO_2 as possible. The reaction set in at 300° C. and increased slowly up to 450°, after this rapidly. Gaseous mixtures containing 19 to 26 per cent. SO_2 by volume were employed (such high concentrations of SO_2 never occur in practice). In the case of gases containing 11 to 16 per cent. SO_2, a stronger reaction did not set in before 560°; at 569° 90 per cent. had been transformed. Altogether the principal point is the concentration of SO_2, whilst those of O_2 and H_2O_2 are not very important. But the concentration of the aqueous vapour is of considerable influence. Even if no oxygen whatever was present, sensible quantities of HCl were formed, which leads to the conclusion that some sulphite was formed, which, as the analysis of the residue shows, partly changes into sulphate and sulphide:

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[1] *Chem. Ind.*, 1905, 28, 173, 198, and 226.

$$4Na_2SO_3 = 3Na_2SO_4 + Na_2S.$$

About 2 vols. HCl are formed to 1000 vols. SO_2. SO_2 also liberates a corresponding quantity of HCl, corresponding to the equilibrium:

$$2NaCl + H_2O + SO_2 \rightleftarrows Na_2SO_3 + 2HCl.$$

Some experiments seemed to show that in the presence of an excess of oxygen, sulphuric acid is not formed in the first instance, and that therefore such a preliminary formation can have no fundamental importance in the Hargreaves process. Other experiments showed that at the temperatures which come into question in this case, sodium sulphite is instantly transformed into sulphate. Keppeler's idea is that primarily sulphite is formed, certainly at first only in small quantity corresponding to the above-mentioned equilibrium, but that is continuously reformed, as the sulphite at once passed over into sulphate. Further experiments showed that the mixtures of sodium chloride and sulphate, formed in the Hargreaves process, begin to soften at 610°, independently of their composition. It is not advisable to go beyond this point, for reasons already mentioned; but on the other hand, the temperature should not be too low, since then the speed of reaction is too small. It will be best to work between 500° and 550°—that is, at a just visibly red heat (525°).

The conclusion from Staedel's experiments that the formation of sulphuric acid is not an intermediate stage in the process suggests doubts of the value of a late patent of J. Hargreaves (Fr. P. 384144, of 1907) according to which the decomposition of sodium chloride by a mixture of sulphur dioxide, steam, and air, resulting in the formation of sodium sulphate and hydrochloric acid, is accelerated by the addition of certain salts or oxides, such as those of copper and iron, which act as catalysts, facilitating the conversion of sulphurous into sulphuric acid. The catalyst (oxide, hydroxide, or salt, or iron or copper) may be mixed with the salt, and the mixture made into briquettes, which are preferably grooved or perforated, or the catalyst, in the form of iron or copper chloride, may be volatilised, and the vapour mixed with the gases employed. The briquettes are stacked in the decomposition chamber in columns, the upper portions of which are supported so as to prevent crushing near the base. The catalyst should be very intimately mixed with the salt and is, therefore, preferably added in the form of a solution, and its amount may vary from about 0·1 to 1 per cent. according to the desired purity of the product.

Raw Materials.

The kind of salt is of great importance, both chemically and mechanically. From a mechanical point of view the fine-grained "butter-salt," obtained in the salt-pans at a *boiling*-heat, is the best; the ordinary "common salt" is too coarse-grained, and gives too loose cakes. Rock-salt, merely crushed, is unsuitable, but it is all right when finely ground. With fine-grained salt, hard cakes are obtained which form but little dust in the cylinders, and which are much more regularly and quickly transformed into sulphate than coarse-grained salt. The process is much more quickly finished with finely ground rock-salt than with pan-salt. In the former case sometimes chemical reasons are superadded to this. The ferric oxide, generally occurring in English rock-salt, acts as a carrier of oxygen; a recent patent (see below) actually prescribes the addition of ferric oxide, where this causes no inconvenience in the use of the saltcake. It has also been asserted that the calcium sulphate and clay, contained in rock-salt, promote the decomposition; but this is questionable.

At all events it has been found most suitable to add to the ordinary common salt (pan-salt) a certain quantity of finely ground rock-salt; preferably 70 or 75 of the former with 25 or 30 of the latter is employed, and this yields saltcake not exceeding 0·5 per cent. of NaCl. For the use of glassworks this saltcake contains too much iron; for these saltcake is made from pan-salt alone, and therefore costs rather more; the cylinders in this case take a much smaller charge, and yet require a third more time for finishing (*cf.* below).

Morrison emphatically cautions operators against occasionally charging one or two of the cylinders, which otherwise work with the above mixture of pan-salt and rock-salt, with common salt alone, or *vice versâ*.

Practically, the cheapest obtainable common salt is employed, such as the waste from trimming the salt bricks, dirty salt, etc.

Preparing the Salt.

The proper preparation of the salt is the keystone for the success of the Hargreaves process. The salt ought to possess a sufficient degree of porosity to make it completely permeable to gases; and it ought also to fill the large chambers in such a way that the gases must traverse it quite uniformly. It cannot possibly be employed in the state of powder, because then the gas would not penetrate through it at all, especially after a crust of sulphate had been formed; it must therefore be formed into lumps. These lumps must be sufficiently strong to bear the pressure of the superjacent mass, and yet porous enough to be penetrated by the gas to their innermost core and to be completely converted into saltcake. The solution of this problem was only accomplished after several years; and the extension of the process was greatly retarded by this difficulty. Apart from Hargreaves' patents, attempts to obtain the salt in a suitable form were made by Hunt (B. P. 2016, of 1874), Brock (B. P. 1502, of 1875), Milburn and Jackson (B. P. 1917, of 1875), M'Dougall (B. P. 3003, of 1875), Stevenson (B. P. 1723, of 1875), and Hawksley (B. P. 3789, of 1880).

In the end, the drying process was carried out successfully by the employment of the continuous apparatus first proposed by Mr Stevenson, but greatly improved by a mechanical contrivance patented by Mr Hargreaves. The damp salt is continuously dropped from a hopper on to a row of metal plates connected so as to form an endless chain, which passes through an oven of 5 ft. width and 40 to 130 ft. length; the heating is done by fire-gases traversing the interior of the oven. Before the end of the plate-chain enters the oven, the salt is pressed down upon it by means of shovels, or mechanically by a roller, and thus converted into a flat cake. At the other end of the oven, where the plate chain carrying the dry salt comes out, the cake is broken into pieces by hand or by machinery.

The heating from above is a most essential advantage of this process. It causes the formation of a hard crust on the top, and the adhesion of the salt at the bottom to the plates, formerly very troublesome, when the firing was done from below, is no longer to be feared.

The Production of Sulphur Dioxide.

In principle this is performed just as in the manufacture of sulphuric acid. But for the Hargreaves processes the pyrites-burners are constructed with a special regard to losing as little as possible of the heat generated in them. For this purpose they are always placed in two rows, back to back

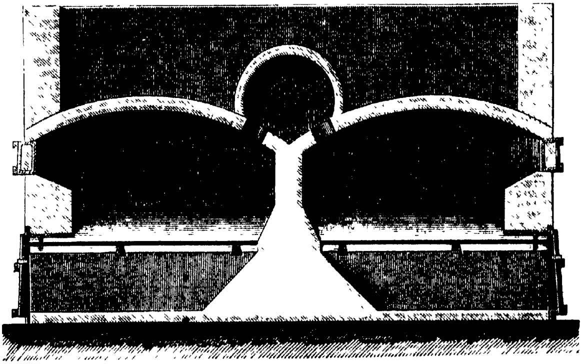

FIG. 61.

and with outer walls 2 ft. thick. The walls consist of common bricks, lined with a half-brick thickness of firebricks. This is done not merely for cheapness, but because the common bricks conduct the heat better than firebricks. Probably Falding's hollow walls (B. P. 17602, of 1893) would be very useful here. The iron parts should be as little as possible exposed to the action of the hot pyrites, in order to avoid cooling; the charging-doors are therefore lined with fireclay, etc. The burner arch descends at the back more than in front; in the channel formed by the junction of the two arches the gas-flue is arranged. This flue, as well as the arches, is covered with ashes at least 2 ft. deep; this is rendered possible by making the front walls so much higher. Fig. 61 gives a transverse section of Hargreaves's pyrites-burners to illustrate the above.

The burners are mostly built in the manner usual on the Continent, communicate freely at the top and have only a single arch, the divisions between the single burners not extending above the charge of pyrites.

The burners differ from ordinary pyrites-burners in the fact that the *steam* is introduced into the hot burner-gas, either in the gas-space above the burning pyrites, by means of a steam-pipe passing through the arch, or into the large metal pipe which carries the gas from the burners to the cylinders. It must be superheated and at the same time completely dried.

The composition of the burner-gas (apart from the never-absent SO_3) has been given on p. 200.

Apparatus for decomposing the Salt (Cylinders).

The salt, prepared in the manner previously described, is placed in cast-iron cylinders, where it remains without further manipulation till converted into sulphate. The minimum number of cylinders is eight; the greater the number, it was formerly believed, the more regular is the reaction, and the smaller the quantity of fuel required per ton of sulphate manufactured. In fact, as many as twenty cylinders were employed. More recently opinions changed on this subject; the large sets were cut in two, and sets of eight cylinders, six of which were working, and two being discharged and recharged, were considered best. The series of cylinders was so arranged that each in its turn became the first, intermediate, and last. The sulphurous acid was first admitted into the cylinder whose contents were most nearly converted into sulphate; and the spent gases passed out from that which was last charged with salt, after passing through a succession of cylinders containing less and less sulphate.

The older sets (before the year 1880) had cylinders of 15 ft. diameter, but 18-ft. cylinders were usual.

The working-drawings of a Hargreaves apparatus as used in 1890 were supplied through the kindness of Mr John Morrison, chemical engineer, of Newcastle-on-Tyne, to whom as well as to Mr John Hargreaves thanks are due for further information thereon. The drawings represent a set of ten 18-ft. cylinders.

Fig. 62 shows a partial side-view of the cylinders, with the drying-oven and the preparatory apparatus, the latter merely sketched on account of the small scale. A, steam-engine; B, saltmill with the elevator C; D, mixing-box; E, stamps; F, longitudinal and cross cutters; F′, drying-oven, with the carrier G; H, the brickwork surrounding the cylinders, of which only the discharging-holes *a a* are visible.

Fig. 63 shows a set of ten cylinders—each 18 ft. diameter and 12½ ft. high, and each of which furnishes about 55 tons of saltcake—in different horizontal sections, viz.: at A B, through the foundations; at C D, just above the bottom, below the grates; at E F, above the grates; at G H, seen from above, with the burner-gas pipe, the charging holes and gas-pipes being cut through. Fig. 64 shows a longitudinal section through a cylinder.

The cylinder-shell is built up from two rings. The bottom consists of four segments, dovetailed in a special way (*cf.* the later patents), which causes it to stand very well. Fifteen inches over the bottom a grate, *a*, formed by a number of perforated plates, is placed. The charging and discharging arrangements appear to be the

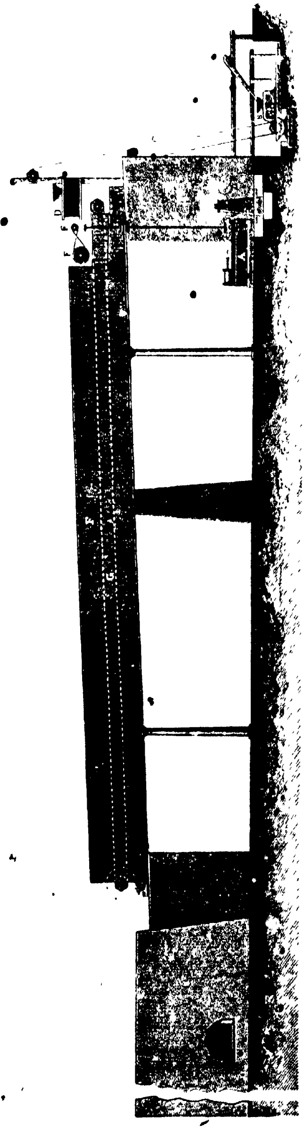

FIG. 62.

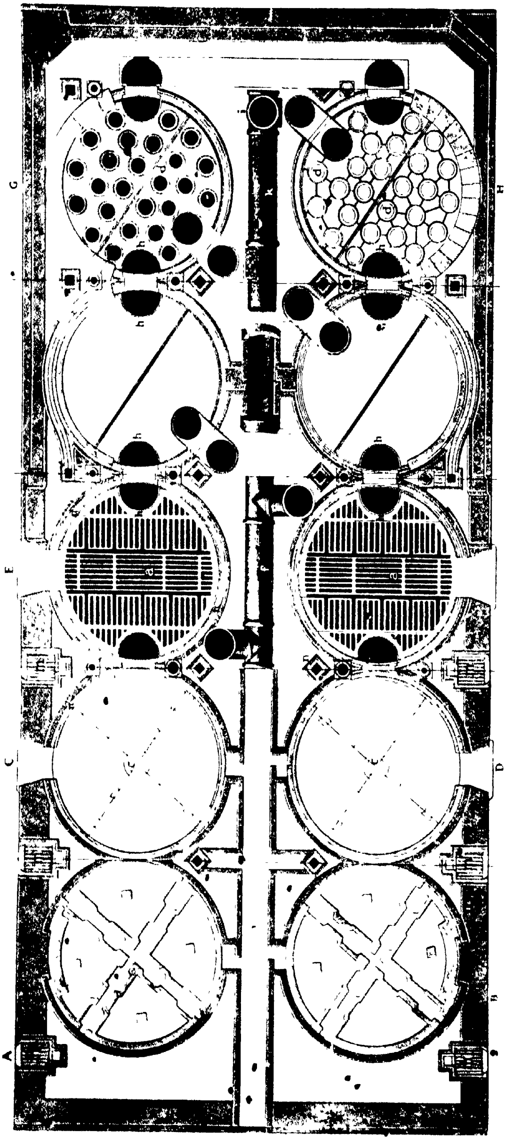

FIG. 63.

weakest parts of the design. Three days are required from the time when a cylinder has been put out of series for discharging, to the time when it has been recharged and is again ready for work.

Mechanical discharging apparatus was also tried but was not successful, as the saltcake remained behind in the back parts of the cylinders.

In the centre of the cylinders there is a hollow pillar, *c*, 10 in. wide, which passes through the grate down to the bottom; the foundations are made in such manner that the foot of *c* rests indirectly on a brick pillar. On the top, just below the cover, *c* is provided with a flange, serving as a support for the points of the sectors composing the cover; pipe *c* itself continues above this and projects 2 ft. above the layer of ashes covering the cylinder-top; it is closed by a loose cap. By means of this central pipe *c* it is possible to examine the temperature of the mass at various depths (which is mostly done merely by observing the degree of glowing), and also to introduce cold air in case the mass becomes overheated.

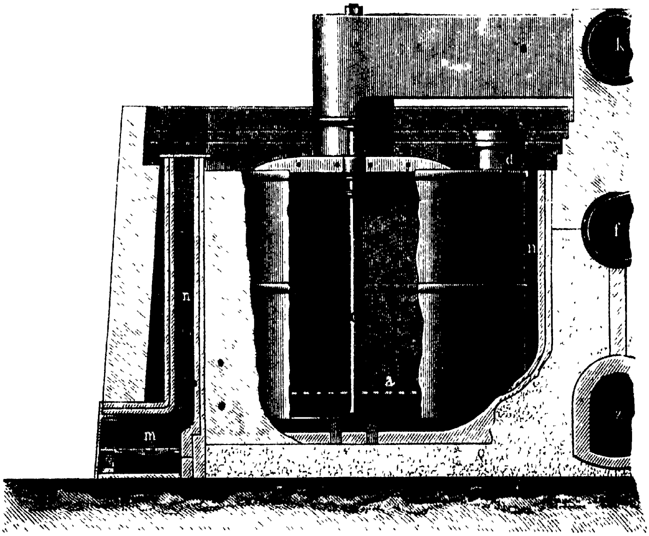

FIG. 64.

On the cylinder-cover there is a large number of necks, *d d*, serving for charging the cakes of salt into the cylinders. The outer wall projects above these necks, so that the cylinder-tops can be kept covered with a thick layer of salt, which in this case is preferred as an insulator to ashes, because it prevents any dirt getting into the cylinders.

The burner-gas, consisting of SO_2, O, H_2O, and N, is conducted through the 3-ft. metal main-pipe *f*, running between the two rows of cylinders and embedded in a deep layer of ashes. From this main the branch-pipes start for each cylinder, and allow the gas to enter the cylinders through valves. Only one of these valves is open at a time, viz., that belonging to the cylinder forming the first member of the series, in which the decomposition of the salt is nearly finished. The fresh burner-gas thus enters exclusively into this cylinder, from above. At the bottom the gas goes away by the lateral pipes *h h*, cast in one piece with the cylinders, and enters into the next cylinder from above. The same is the case with all other cylinders; only in the last of the series the lateral pipe is closed against the next cylinder, and here the exit gas (now containing only HCl in place of SO_2) must make its way through *i* into the hydrochloric-acid flue *k*.

We thus find in every cylinder on one side a long pipe, *h*, reaching down below the grate, and on the diametrically opposed side a short pipe, *h'*, ending just below the top. The cylinders are placed close together, so that a long pipe, *h*, is always close to a short pipe, *h'*, and a short connecting-siphon (*cf.* below) suffices for putting them into communication. Only at the two ends of the set a long connecting-pipe must be used. Thus the whole system might be converted into a continuous annular channel, which, however, is never done. But it is also possible to interrupt the connection at any given place, and to connect by another siphon the short pipe *h'* with the burner-gas main *f*; this makes each cylinder in turn the first of the series, whilst at the opposite end of the series the long pipe *h* is put into communication with the hydrochloric-acid flue *k*. Just in the same way each cylinder, or some of them, may be isolated, and those before and behind it may be connected with the pipes for SO_2 and HCl.

The connecting-pipes employed are shown in Fig. 65. They contain valves *a a*, which are made tight by means of the heavy iron door *c*, manipulated through the small manhole *b*, plate *c* resting on an inclined frame, planed and faced at the point of contact with the door.

The hydrochloric-acid gas is carried away by a pipe, *k* (Fig. 64), placed above.

The cylinders must be heated externally in order to get them up to the temperature required for the reaction, and to keep them at this during the whole time of decomposition, which may amount to four weeks. This was certainly no easy task to perform with apparatus of such extraordinarily large sectional area, and it would be practically impossible if the mass was not most efficiently heated from within, firstly by the proper heat of the burner-gases passing through, and secondly by means of the heat liberated in the cylinders themselves by the chemical reaction. Calculation shows that of the 143·6 heat-units liberated in the formation of a gramme-molecule of Na_2SO_4, almost exactly three-fourths, viz., 107·4, are set free in the pyrites-kilns, and one-fourth only in the cylinders themselves. At first, so much fuel was used (up to twice the weight of the saltcake) that the economical success of the process seemed doubtful. But later on the quantity of fuel was constantly reduced, by preserving as much as possible

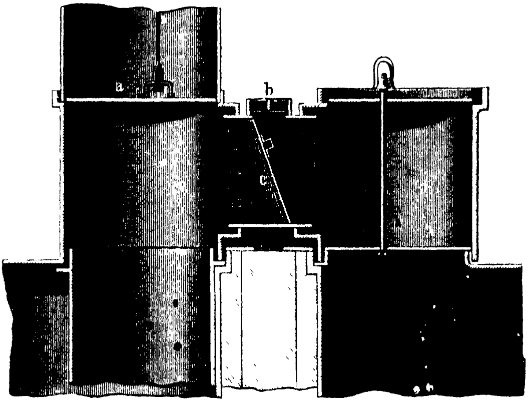

FIG. 65.

the heat of the burner-gases through continually improving the heat-insulation of the burners and gas-pipes and of the cylinders themselves. This aim produced very considerable alterations in the design of the sets of cylinders and connecting-pipes, as will be clearly seen by comparing the plans contained in this and those in the first edition. By all these changes the original consumption of 2 tons of coal for 1 ton of saltcake was brought down to 2½ cwt. In a few places they fire merely for heating up, and when the cylinders have attained their proper heat the fires are shut down.

It is, of course, impossible to make the gases from the burners circulate through all the cylinders from the top downwards, and at last through the condensers, by natural draught. The exit gases, viz., hydrochloric acid and the excess of other gases, are drawn from the cylinder by an *aspirating apparatus.* The most suitable one is a *Root's blower*, made by Messrs Thwaites of Bradford, modified by replacing the wooden revolving pistons with iron ones, the temperature being too high for the wood to stand without injury, apart from the rapid decay of the wood which would be produced by the corrosive action of the gases. The iron pistons and shell of the blower are not injuriously acted upon by the gases so long as the temperature is sufficiently high to retain them in the gaseous state; and the blower receives no more damage than it would from drawing the same volume of atmospheric air through it. This temperature is easily maintained by placing the machine under cover and putting a layer of non-conducting composition, such as is used for steam-boilers, on the outside shell.

If the parts of the machine subject to friction were allowed to attain the temperature of the gas passing through it, very rapid wear would take place; but this is provided against by making the shafts revolve in brass bushes fixed in a hollow bracket. A current of water is kept flowing slowly through the bracket, so as to keep down the temperature of the brasses; but, from the position of the inlet and outlet holes in the bracket, this water has little cooling effect on the shell. No stuffing-box is required, as the very small amount of air leaking through is of no practical importance, and there is no tendency of the gases to leak outwards unless great resistance is placed on the exit side of the blower.

Among the later patents relating to the process, reference may be made to B. P. 2809 of 1879, Ger. P. 17409, and B. P. 5682 of 1886.

Working of the Hargreaves Apparatus.

The salt, mixed in proper proportions (p. 203), moulded into cakes and dried, is charged still hot, if possible, into the cylinder which happens to be empty, by means of the openings in the top, which is a somewhat slow process (p. 210), as these necks themselves greatly impede the traffic on the top of the cylinders. The cylinder in question is then properly closed, and is put in series as the last. A cylinder of 18 × 12 ft., if charged with a mixture of 70 common salt and 30 rock-salt, furnishes about 57 tons of saltcake; or 48 tons, if charged with common salt alone, which produces "refined saltcake"; that is, in the former case 53, in the latter 63 cub. ft. of space are required for 1 ton of saltcake. The transformation requires in the first case three weeks, in the second four weeks. To this must be added the time required for discharging and recharging, so that the producing capacity per twenty-four hours of a set of ten cylinders of the above size (= 31,000 cub. ft.) may be taken equal to 23½ tons of common saltcake (1300 cub. ft. cylinder space per ton) or 15½ tons of refined saltcake (1980 cub. ft. per ton).

If fresh burner-gas direct from the pyrites-kilns were allowed to act upon fresh salts, the reaction would be so violent and the evolution of heat so great that the salt would be fluxed. This is prevented by exposing the fresh salt merely to the last gases, which contained very little SO_2; but here also the temperature must be high enough to ensure the reaction being effected—that is, above 400°. This soon produces a crust of sulphate on the salt, which becomes gradually thicker in the preceding cylinders, so that in the first cylinder the cakes are almost completely transformed into Na_2SO_4. Here, then, the fresh hot burner-gas is introduced, and by its great richness in SO_2 carries the transformation to completion; and, owing to the presence of SO_3 in the burner-gas, even bisulphate would be formed if the prevailing temperature were not above the decomposing temperature of the latter.

There is a rule *that the gases leaving the apparatus should always retain a little* SO_2, say 2 per cent. of the total. If all the

SO_2 is consumed, the oxygen always present in excess must react with the HCl at the temperature in question, and must yield some free chlorine, which would strongly act upon the cylinders.

Besides SO_2 the exit gases always contain a little SO_3. This is no matter of surprise; for under favourable circumstances Na_2SO_4 can be entirely converted into NaCl by HCl.[1] This SO_3 is mentioned in Morrison's analysis of the exit gases.

On the assumption of a loss of 2 per cent. S in the exit gas the yield ought to be $\frac{142 \times 98 \times 100}{32 \times 97} = 448$ parts of 97 per cent. saltcake. But this yield is nowhere attained, and this proves that a certain quantity of sulphur is lost in the shape of bisulphate.

The condensation of hydrochloric acid is, of course, made more difficult by the high temperature of the exit gases (which, however, can be brought down by long strings of tubes), and by the dilution of the HCl gas with such a very large quantity of inert gases that they contain at most 15 per cent., frequently only 10 per cent., of HCl by volume. The Hargreaves gases are much poorer than those from blind roasters, and are more nearly comparable to open-roaster gases. But they have this great advantage over both of these, that they are given off quite continuously, nearly always at the same concentration; and this is of such importance for the condensation that there is no difficulty in coming down to 0·1 gr. HCl per cub. ft. (0·23 g. per cubic metre) in the exit gases from the condensers.

The following analyses of Hargreaves saltcake were supplied from a thoroughly trustworthy source:—

1. From a French works, where rock-salt is used (1883).

	a.	b	c.
Na_2SO_4	91·00	92·00	93·20
NaCl	0·05	0·03	trace
H_2SO_4	0·62	0·88	0·37
$CaSO_4$	3·21	3·40	2·99
$MgSO_4$	1·41	1·42	1·43
Al_2O_3	0·17	0·14	0·18
Fe_2O_3	0·37	0·16	0·25
Insoluble in HCl	0·91	1·08	1·19
H_2O	2·10	0·75	0·30
	99·84	99·86	99·91

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[1] Hensgen, *Ber.*, 1876, p. 1671.

2. From a Widnes works, where common salt is used (1890).

	a. Ordinary decomposing furnace.	b. Hargreaves.
Na_2SO_4	97·3	98·2
SO_3	1·3	0·6
NaCl	0·4	0·2

(*a* is given for comparison with *b*.)

The following *cost account* is given by Morrison; but he says that it referred to the most favourable condition then obtaining (in 1881). He states the consumption of coal per ton of saltcake:

For drying the salt	1 cwt.
„ heating the cylinders	3 „
„ steam	½ to 1 „
Total	4½ to 5 „

Lomas[1] states that in 1880 Hargreaves saltcake cost 32s., that made from salt and sulphuric acid 36s. per ton.

Saltcake Processes similar to the Hargreaves Process.

A patent of Hutchinson's (dated 1st January 1876) proposed the production of alkaline sulphates from their chlorides, by a process similar to Hargreaves and Robinson's, but dropping the chlorides as a spray into a space filled with the highly heated vapours. This was probably never tried practically.

Another variation of Hargreaves's process was patented by Storr, Best & Morris, on 10th April 1877. The gas of the pyrites-burners is to be admitted into the lower portion of a coke-tower, in which a solution of potassium or sodium chloride runs down; at the bottom a solution of sodium sulphate flows out; at the top hydrochloric-acid gas leaves the tower. Similarly Pohl (B. P. 5031, of 1879) passes SO_2 and hot air into a solution of NaCl, in order to produce Na_2SO_4. This modification of the direct process would not work in practice, as the reaction is quite incomplete without an oxygen carrier (*cf.* below).

Pedder (B. P. 4712, of 1891) proposed as an improvement of the Hargreaves process to mix hydrogen chloride vapour with the steam, so as to promote the action of the salt in the cylinders. Further, in order to keep the salt more porous, a little sulphate was to be mixed with it from the first, in the solid or liquid form, so that each lump of salt contains on its surface a certain quantity of sodium sulphate.

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[1] *Manual of the Alkali Trade*, p. 155.

The Chemische Fabrik Rhenania (Ger. P. 73611) renders the salt-blocks more porous and more easily decomposable by mixing with the salt combustible matter, such as coal-dust, peat, straw, or sawdust.

The Société Daguin & Cie (Ger. P. 47990) proposes increasing the energy of the reaction between SO_2, O, H_2O, and NaCl, and lowering the temperature required for it, by adding an oxygen carrier in the shape of the chlorides or sulphates of iron, manganese, copper, or tin [*cf* the older patent of Hargreaves, Robinson & Hargreaves, p. 198, and that of J. Hargreaves, below]. If MnO_2 is employed, free Cl is obtained. It is possible to work with aqueous solution, *e.g.*, a solution of 250 kg. common salt, mixed with the equivalent quantity (370 kg.) of $MnCl_2$, to be treated at a boiling heat with 10 per cent. SO_2 gas [which is never obtained by burning pyrites!] and air. The reaction may be represented as taking place in two stages, $MnCl_2$ being re-formed in the second:

1. $2NaCl + MnCl_2 + SO_2 + O + H_2O = MnSO_4 + 2NaCl + 2HCl.$
2. $MnSO_4 + 2NaCl + 2HCl = Na_2SO_4 + MnCl_2 + 2HCl.$

[Supposing these reactions to occur, it seems hardly possible to separate the sodium sulphate in the anhydrous state without losing much of the manganous salt, which also acts as an impurity in the sulphate.]

Bassett and Baranoff (B. P. 21447, of 1894) produce the SO_2 intended for decomposing the NaCl as follows:—Calcium sulphate (natural or artificial) is mixed with carbon and heated in a retort; the CO_2 given off is utilised later on. The calcium sulphide formed is moistened with water, and is then subjected, in an apparatus similar to that used for making bleaching-powder, to the CO_2 from the first reaction. The H_2S evolved is burned to SO_2 and utilised for decomposing NaCl. The residual calcium carbonate is roasted for the liberation of the CO_2 it contains.

Reiss (Ger. P. appl. R15277) adds to the sodium chloride intended for the Hargreaves process a sufficient quantity of sodium sulphate to prevent a fluxing of the mass during the process (*cf.* Pedder's B. P. of 1891).

A. Clemm (Ger. P. 115250) aims at the same object by the addition to the common salt of 5 to 10 per cent. of clay, gypsum, etc. The saltcake thus obtained can be used directly for glass-making, etc., or else refined by dissolving (Chapter VI.).

J. Hargreaves (Fr. P. 384144. of 1907) promotes the reaction by the catalytic action of copper or iron salts, mixed with the common salt before moulding. Of these substances from 0·1 to 1·0 per cent. is used, according to the degree of purity required. The action of ferric oxide, and even more so of cupric oxide, as oxygen carriers in the Hargreaves process has been also pointed out by Krutwig and Dernoncourt.[1] The best yields were obtained at a temperature of 500° C. (*cf.* the patents of Hargreaves, Robinson & Hargreaves, p. 198, and of Daguin, p. 217).

According to L. P. Basset (Fr. P. 477353, of 1914), sulphur dioxide may be caused to react with sodium chloride when the latter salt is in the state of vapour, or in the finely divided state produced by condensation of the vapour. The sulphur dioxide may be mixed with an excess of dry air, in which case sodium sulphate and chlorine will be produced, or an excess of air and steam may be employed, in which case sodium sulphate and hydrogen chloride will be obtained. The sodium chloride is volatilised in a furnace surmounted by a dome, or connected with a chamber, in which the reaction between the volatilised chloride and the sulphur dioxide can occur; or the sodium chloride may be volatilised in the furnace in which the sulphur dioxide is produced. The process may also be combined with the manufacture of cement from calcium sulphate, clay, and carbon, sodium chloride being mixed with the cement raw materials, and a blast of air introduced into the rotary kiln about half way along its length. The Salzwerk Heilbronn A.-G., and P. Brandenburg Heilbronn (Ger. P. 295074, of 1915) propose to spray fused alkali chloride by means of sulphuric acid, or a mixture of sulphuric acid with air or steam, or with sulphur dioxide and steam. Decomposition occurs with the liberation of hydrochloric acid, and alkali sulphate is precipitated as a fine powder.

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[1] *Rev. trans. chim. Pays-Bas*, xvi., 173; xvii., 349.

Statistics relating to Saltcake.

The following statistics (R. C. Wells, *Mineral Resources of the U.S.*) show how the production of saltcake in the United States is declining:—

	1917 Short tons.	1918 Short tons.	1919 Short tons.
Saltcake	183,909	141,054	134,685
Glauber's salt . .	47,757	50,715	42,087
Nitre-cake . . .	387,821	143,155	83,402

Applications of Sodium Sulphate.

At one time most of the sulphate of soda manufactured was consumed as an intermediate product in alkali-making. Nowadays, little if any is used for this purpose.

The glass-making industry now consumes far more sodium sulphate than was formerly used for the Leblanc process. The purer article is used for plate-glass and white bottles, the crude article for sheet glass and green bottles. Other applications are: for making ultramarine; for Glauber's salt; for impregnating seeds as a protection against rust[1]; for decomposing the calcium chloride in the mother-liquors of saltpetre works; for decomposing calcium acetate in making sodium acetate; for manufacturing the hypochlorite, thiosulphate, and several other salts of sodium from the corresponding calcium salts. Eitner[2] states that calcined sodium sulphate is very good for preserving green hides.

The crystallised salt is employed in medicine, especially for veterinary purposes, and in chemical laboratories for freezing mixtures. It finds application also in the dyeing industry.

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[1] *Wagner's Jahresber.*, 1856, p. 189.

[2] *Ibid.*, 1880, p. 805.

calcium
ontain

CHAPTER VI

MANUFACTURE OF PURE SODIUM SULPHATE AND GLAUBER'S SALT

BY far the greatest quantity of sodium sulphate is used in an impure state as the anhydrous salt. The usual standard required of the commercial anhydrous salt is that it shall contain 95 per cent. of sodium sulphate, and in many cases there is no stipulation as to the nature of the remaining 5 per cent. Very often it is required that the iron content be low, *e.g.*, for the manufacture of plate-glass. It is often possible to attain a sufficient degree of purity by careful choice of raw materials and by using lead pans for the decomposition, but when the sodium sulphate cannot be obtained sufficiently pure in this way, it must be purified. When pure sodium sulphate or Glauber's salt is to be made from the impure saltcake, this purification is always performed by dissolving, precipitating the impurities, separating the liquor from the precipitate, and obtaining the desired product from this solution. The details of the process vary considerably according to the scale on which it is carried out and on the degree of purity desired. A pure product is necessary for the manufacture of plate-glass, for paper pulp works, and for pharmaceutical purposes. If it is to be used for pharmaceutical purposes it is particularly important to obtain a product free from arsenic. For plate-glass and paper making it is important to remove iron as completely as possible, since even traces of iron impart colour to the finished article. Crude saltcake usually contains 0·1 to 0·3 per cent. of iron, but sometimes more. By refining, this can be reduced as low as 0·006 per cent. The French plate-glass manufacturers require a guarantee that the amount of iron in the saltcake does not exceed 0·017 per cent. Fe and, for such purposes, saltcake is sometimes purified on a large scale.

Manufacture of Pure Anhydrous Sodium Sulphate.

The older method for the manufacture of pure anhydrous sodium sulphate was to prepare pure Glauber's salt which was then dehydrated. The preparation of pure Glauber's salt, which is the first stage in this process, is described later in this chapter. From the pure Glauber's salt, the anhydrous salt is prepared by drying. Glauber's salt loses water very readily by efflorescence in a warm dry atmosphere, and on a small scale it is often prepared by heating on a hot steam plate. This method is, however, not suitable for large scale manufacture. Glauber's salt contains, as water of crystallisation, nearly 53 per cent. of water, and the desiccation of this, if attempted on a large scale, would be a difficult problem. There is, however, no need to isolate the Glauber's salt, since a solution of sodium sulphate deposits the anhydrous salt if evaporated at any temperature above 32·4°. The plant used varies considerably, mainly according to the degree of purity required in the finished product, but the process is practically the same in all cases. The crude saltcake is dissolved at a temperature of about 35°, as the maximum solubility of the salt is a little below this temperature. Small quantities of lime and bleaching powder are added and the mixture well stirred. When all the precipitate has settled, the clear liquor is drawn off and evaporated. As the evaporation proceeds, the crystals of anhydrous salt are raked out and drained. The last of the water is expelled by heating these crystals.

Where it is not necessary to obtain a product of the highest purity, the plant and procedure described by Jaeckel[1] may be used. Water is heated by steam in iron tanks each about 4½ by 4 by 3 ft. and the saltcake placed in sieves suspended in these tanks. To each tank, containing about 8 cwt. of saltcake in solution, about 28 lb. of lime is added as a thick sludge, and the mixture thoroughly stirred. (It is usual to add also at this stage a few pounds of bleaching powder.) After standing for four hours, the clear liquor is drawn off from the brown mud by means of lead siphons. The mud is washed with hot water and the washings used to dissolve the next batch of saltcake. The liquor is boiled down in pans 8 ft. long, 5 ft.

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[1] *Dingl. polyt. J.*, 161, 169.

wide, and 1½ ft. deep. The sludge of small crystals formed as the evaporation proceeds is raked out and drained. This is then dried in reverberatory furnaces where it cakes into hard lumps which are ground to powder in a mill. The evaporation and final drying are sometimes combined by evaporating in shallow pans, heated from above by the direct heat from the flame gases. The crystals are raked on to a shelf at the side of the pan where the final drying occurs.

With plant such as is described above, it is inevitable that some iron scale and flue dust will get into the final product, and unless great care is exercised the product may be far from pure. When a very pure product is desired, the saltcake is dissolved in lead-lined wooden vats, heated by open steam. The amount of lime and bleaching-powder necessary to precipitate completely all iron and other impurities is readily found by experiment. If the solution is left slightly acid, the colour is better but the salt more readily takes up iron during the drying, and the final product is likely to be worse than if sufficient lime is added to make the solution faintly alkaline.

It is not easy to remove the last of the water from the purified sodium sulphate without introducing ash or iron. It has been proposed to centrifuge the crystals as they are removed, and thus reduce the amount of drying. The usual process is to dry in a gas-fired reverberatory furnace of simple construction. Provided care is taken to use clean gas, an entirely satisfactory product is obtained.

Hermann (B. P. 13983, of 1887)[1] describes the process outlined above, evaporates in pans with mechanical agitation, and centrifuges the moist sulphate. The pan is so arranged that the smoke and flue gases cannot come in contact with the liquor.

Péchiney's process for the preparation of anhydrous sodium sulphate has already been described (p. 193). This process is said to yield a product containing chloride.

Pure Crystallised Glauber's Salt.

The preparation of pure crystalline Glauber's salt is considerably easier than the preparation of the anhydrous salt.

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[1] The apparatus is also described in *J. Soc. Chem. Ind.*, 1888, p. 674.

The crude saltcake is dissolved in water, heated by open steam, in lead-lined wooden vats. The amount of saltcake dissolved should be sufficient to yield a solution with a density of 1·14 to 1·15 at 30°. The flocculent brown precipitate produced by the addition of lime and bleaching-powder is allowed to settle and the clear liquor drawn off by means of lead siphons. It is advisable to have a small lead steam pipe inside the lead siphon in order to clear it quickly should the salt crystallise in the siphon. The sludge is washed and the washings used to dissolve the next batch of saltcake. The clear liquor is then allowed to crystallise by cooling in flat lead-lined tanks. The area and depth of these must be determined largely by the size of the crystals required and the mean temperature of the atmosphere. No Glauber's salt will separate unless the temperature is below 30°, and as heat is liberated in the crystallisation the crystals separate very slowly in warm weather. If the solution is left faintly acid, the crystals are colourless even if a trace of iron be present, but the acidity must be kept very low or traces of lead will be found in the product. Iron vessels are sometimes used for the crystallisation but are not recommended as the product is often contaminated with iron, particularly if the solution is acid. It is usual to place a considerable number of wooden strips in the vessel, as otherwise the crystals build up into solid masses on the walls of the vessel.

At one time considerable attention was directed to the conditions for obtaining Glauber's salt in such crystalline forms that it could be used for adulterating other salts. The three forms in which it could be obtained were known as "mock Epsom salts," "imitation soda," and "needle crystals." The "soda" crystals are readily obtained by the slow undisturbed cooling of a large volume of liquid in a deep vessel. The crystals obtained in this way resemble washing-soda crystals. In order to obtain crystals which could be sold as "best Scotch soda," 12 parts of soda-ash was added to 100 parts of salt-cake and gave crystals closely resembling washing soda.[1]

If the crystallisation is disturbed, small needles are obtained. When these are required, the liquid is kept slowly moving by a stirrer, and the salt is obtained as needles which resemble Epsom salts and have been used for its adulteration.

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[1] *Chem. News*, 16, 227.

If the "needle crystals" are required, the crystallisation is conducted in shallow pans containing only about 1½ in. depth of liquid (about 1·14 density at 30°). Cooling must be rapid, and there must be no disturbance of the liquor during crystallisation. These crystals are made only for pharmaceutical purposes as they are more expensive to prepare than the other forms.

In order to reduce the cost of the plant, iron vessels are often used as crystallisers, but these, before use and every time they stand empty, must be scoured bright with a brick or with pumice; and in spite of this, rust spots upon the crystals adhering to the sides cannot usually be avoided. The rusting can be prevented by painting the well-scoured and dried surface with a double coat of iron minium (ferric oxide and clay) and boiled linseed oil, adding some drying-preparation. The paint must be renewed from time to time.

The following process is employed at Stassfurt for making pure Glauber's salt:—The mother-liquor adhering to the crude salt is removed by washing with cold water. The salt is then recrystallised and is obtained in the three following shapes:—

(1) In fine needles, formerly used for adulterating Epsom salts.
(2) Evenly formed thicker needles or prisms for pharmaceutical purposes.
(3) Short, thick prisms, formerly used for adulterating soda crystals.

The third form represents the main bulk of the crystals.

The crude salt is dissolved in mother-liquor (which can be used a long time without being renewed), with addition of water and steam, until the specific gravity, tested at 40° C., is 1·255. The liquor is allowed to settle for an hour and is then run into wooden or lead-cased iron coolers, which must be at least 2 ft. deep, to form larger (1-in.) crystals. The crystallisation is promoted by suspending smooth wooden laths or strips of lead in the coolers; this is better than strings weighted with pieces of lead, from which the crystals easily detach themselves, and by agitating the liquor cause the formation of fine needles. In wooden vessels, the crystallisation lasts in winter five to ten days, in summer ten to twenty days. After running off the mother-liquor, the crystals are detached with wooden slices and are thrown by means of wooden shovels on to the drainers, where they are washed with water. If the crystals are to retain their brilliancy they must be dried below 35°. This may be done on shelves placed on a flue, and covered with metal plates, or the proper temperature may be obtained by the assistance of steam-pipes. The cost of recrystallising in the form of large hard crystals and drying is from 15s. to 20s. per ton. For making 1000 kg., one requires in summer 1150, in winter 1080 kg. of crude salt. The packing in casks, lined with blue paper, costs 20s. per ton. (Pre-war costs.)

For making salt in smaller crystals, the solution is saturated at 34° C. (1 part Glauber's salt to 3 of water), settled with addition of a little milk-of-lime, and cooled. If the crystals are to be quite fine, the liquor is now and then stirred up.

Glauber's salt entirely free from iron is made from crude salt, according to Schmalz and Lowig (Ger. P. 23378), by treating it with concentrated hydrochloric acid. The temperature is greatly lowered and about half the sodium is precipitated as NaCl, the other half remaining in solution as $NaHSO_4$. This solution is added to a boiling solution of kieserite, saturated with NaCl, and is filtered hot over ground rock-salt. Glauber's salt, free from iron, crystallises out on cooling, and other salts, together with NaCl and $MgSO_4$, remain in the solution, which is employed for making up the kieserite solution. This process, in which a large quantity of hydrochloric acid is lost, is evidently much too dear.

Löwig & Co. (Ger. P. 25777), propose to remove the iron by electrical deposition, using the lead lining of the crystalliser as one electrode and a sheet of copper or iron as the other.

CHAPTER VIII

THE MANUFACTURE OF HYDROCHLORIC ACID FROM CHLORINE

FOR a century the main source of chlorine has been hydrochloric acid, but recently the tables have been turned. The constantly increasing production of electrolytic chlorine has led to an over-production of this material, and it is now very largely used for the manufacture of hydrochloric acid. The methods used fall into four main groups :—

(1) Direct combination of the chlorine with hydrogen.
(2) Interaction with steam in presence of a catalyst.
(3) Interaction of chlorine, water, and carbon.
(4) Interaction with an organic material containing hydrogen
(5) Simultaneous production of hydrochloric and sulphuric acids from chlorine, steam, and sulphur dioxide.

Of these, the first is that most generally employed at present. It presents few difficulties, gives a pure acid, and provides a use for the electrolytic hydrogen which is usually available in the factory where the chlorine is produced. Electrolytic hydrogen is, however, of considerable potential value, and it seems highly probable that it would be used for some other more remunerative purpose than the production of hydrochloric acid if chlorine could be made into hydrochloric acid by some other cheap process. The main attraction of the fourth group of processes lies in the value of the organic by-products obtained in most of these processes.

(1) *Hydrochloric Acid from Chlorine and Hydrogen.*

Hydrogen and chlorine do not combine at atmospheric pressure in the dark. In diffused daylight, gradual combination takes place, whilst in a bright light combination occurs with explosive violence. It has been found[1] that the presence of moisture is necessary for combination to occur, and that there is a definite time interval before combination is rapid. There is considerable evidence that an intermediate compound, probably of chlorine and water, is formed.

Experiments on the influence of temperature on the combination of hydrogen and chlorine have given very discordant results, apparently because of the surface effect of the containing vessel. The mixture has been heated to 440° without explosion, but under different conditions has exploded at 150°.

An investigation of purely scientific character on the slow combination of chlorine and hydrogen at higher temperatures, which showed very complicated conditions, has been made by Sirek.[2]

Hydrogen may be burned in an atmosphere of chlorine, or chlorine in hydrogen. The combination is strongly exothermic:

$$H, Cl = 22{,}000 \text{ cals.} + 0.9\,t.$$

Naturally precautions are necessary to prevent mixing of the gases prior to starting the regular burning. As it has long been known that chlorine can, with proper precautions, be burnt in hydrogen or *vice versa*, recent work and patents are directed mainly to defining conditions or suggesting catalysts which ensure that the combustion proceeds without detonation.

H. and W. Pataky (Ger. P. 114219, of 1900) pass a mixture of chlorine and hydrogen containing rather more of the latter than is required to form HCl, into an apparatus containing coarsely ground wood-charcoal, heated in a water-bath. The gases combine to form HCl by the surface action of the charcoal, which absorbs the gaseous HCl before a detonation can take place. When the maximum of HCl has been fixed by the charcoal, the HCl further formed drives out that which has been previously absorbed in the charcoal.

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[1] Draper, *Phil. Mag.*, 1845 [iii], **27**, 327, and previous papers; P. V. Bevan, *Phil. Trans.*, 1903, A, **202**, 71; Bunsen and Roscoe, *Phil. Trans.*, 1857, **147**, 355, 381, 601; Pringsheim, *Wied. Annalen*, 1887, **32**, 421; H. B. Baker, *Trans. Chem. Soc.*, 1894, **65**, 611.

[2] *Z. physik. Chem.*, **61**, 545; *Chem. Centr.*, 1908, **1**, 1520.

Hoppe (Ger. P. 166598, of 1905) causes a mixture of chlorine and hydrogen to act upon metallic chlorides, decomposable at high temperatures by means of water.

In a later patent, Hoppe (Fr. P. 418731, of 1910) is more specific, and describes a process depending on the alternate hydrolysis of stannous chloride and re-formation of the normal salt In practice the stannous chloride is to be used as a catalyst for the reaction between chlorine and water.

J. L Roberts (Ger. P. 194947) passes molecular (or nearly molecular) quantities of chlorine and hydrogen by separate pipes into a mixing chamber, where they combine at once with production of a flame. That chamber may have the shape of a Y, the gases entering through the two branches. If the gases issuing in the beginning from the third limb are ignited, the flame goes back to the point where the gases meet, and here quietly burns on, with formation of a continuous stream of HCl. The combination is perfect, and furnishes at once pure hydrochloric acid.

Soc. Italiana di Electrochimica (Eng. P. 24024, of 1914) manufacture hydrochloric acid by burning hydrogen in chlorine, or *vice versa*. The cylindrical combustion chamber has a dome-shaped roof through the centre of which passes a pipe leading to an aspirator, and a number of observation-windows made of transparent quartz. Hydrogen admitted through a pipe in the middle of the base passes into a central box, from the top of which it issues through eight burner nozzles arranged in a circle. Surrounding this is another box fitted with seven nozzles which supply the chlorine, the inlet tube for which passes into the chamber through a pipe in the side-wall near the base. The hydrogen is first ignited in the air initially in the chamber, the gaseous products are drawn off, and then the chlorine is admitted. The supply of both gases can be regulated, there is no risk of explosion, and if the temperature gets too high the chlorine may be diluted with air or with an inert gas.

Gibbs (U.S. P. 779998, of 1905) proposes to make hydrochloric acid by combination of hydrogen and chlorine using an excess of hydrogen.

Engelstad (U.S. P. 1121910, of 1914) also uses an excess of hydrogen, but adds also a little air in order that the combination of hydrogen with oxygen may maintain the main reaction. The excess of hydrogen serves to reduce the temperature of the combustion chamber.

Garner and Clayton (U.S. P. 1220411, of 1917) heat a mixture of moist hydrogen and chlorine, in the volumetric ratio of about 50:35, to a temperature not below 340° C. in the presence of wood charcoal, and the hydrogen chloride produced is absorbed in water.

(2) *Hydrochloric Acid from Chlorine and Steam.*

It is well known that chlorine interacts with water to give hyphochlorous acid, which decomposes, yielding hydrochloric acid and oxygen :—

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl.$$
$$2HOCl = 2HCl + O_2.$$

These reactions proceed slowly under all conditions, but the formation of hydrochloric acid in a chlorine solution is readily observed, particularly if the solution is exposed to sunlight. A catalyst which will cause the formation of hydrochloric acid from chlorine and water to proceed at a fast rate would be of great value. So far no satisfactory catalyst has been found, though several patents have been taken out in which carbon is described as a catalyst for the reaction. It is probable, however, that in all cases the carbon is used up in the process, though its function may be partly that of a catalyst.

(3) *Hydrochloric Acid from Water, Chlorine, and Carbon.*

The nature of the reaction between chlorine, carbon, and water probably varies with the conditions, but under most conditions the reaction proceeds according to the equation—

$$2Cl_2 + 2H_2O + C = 4HCl + CO_2.$$

No oxygen is liberated, the whole of it combining with the carbon.

The earlier workers in this sphere all worked at high temperatures, under conditions which gave carbon monoxide as the oxidation product of the carbon.

Lorenz (B. P. 25073, of 1894) proposes making hydrochloric acid from free chlorine obtained electrolytically or otherwise by passing the chlorine simultaneously with steam through earthenware retorts, charged with coke, charcoal, anthracite, or the like, and heated to a dark red heat. The reaction $2Cl+H_2O+C=2HCl+CO$ is stated to take place easily and quantitatively; the CO can be employed for heating the retorts.

A. Naumann[1] contradicts these statements made by Lorenz.

On the other hand, Nagel[2] states that hydrochloric acid is formed if a mixture of steam and chlorine is passed through a column of glowing coke which is maintained at about 1000° C. by substituting a blast of air for the mixed gases at regular intervals. The reaction takes place in accordance with the equation $Cl_2+H_2O+C=2HCl+CO$, and fairly pure carbon monoxide is obtained as a by-product.

Peter (U.S. P. 1229509, of 1917) gives different conditions for the same reaction. He claims that hydrochloric acid is produced by adding to chlorine sufficient water vapour to form a mixture showing practically no green colour against a white background (approximately 3 parts of chlorine to 7 parts of water vapour), and leading the mixture over carbon at a temperature between 100° C. and red heat.

H. D. Gibbs[3] has investigated the interaction between chlorine, water, and charcoal, and finds that the reaction

$$2Cl_2+2H_2O+C=4HCl+CO_2$$

proceeds over a very wide range of temperature above 80°, preferably between 80° and 200°, and that large quantities of chlorine can be handled in a comparatively small apparatus.

The best procedure is to blow the steam and chlorine through a large bed of charcoal used for absorbing gases. Small quantities of air may be admitted at the same time to assist in sweeping out the products of the reaction. The reaction is highly exothermic.

Gibbs gives curves showing the velocity of the reaction at 0°, 12°, 25°, and 37·5°, other conditions being constant. In all cases the production of hydrochloric acid slowly increases and then falls off to a point where it remains practically constant. The reaction proceeds much faster at the higher temperatures. Excess of water was found to be advantageous. Great differences were found between the reactivities of various charcoals.

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[1] *Z. angew. Chem.*, 1897, p.197.

[2] *Chem. Zeit.*, 1912, 36, 54.

[3] *Journ. Indust. and Eng. Chem.*, 1920, 12, 538.

There are several patents covering various conditions for carrying out this process.[1]

It seems probable that there is a future for this process as it is probable that more remunerative uses will be found for hydrogen than burning it with chlorine, and there is no doubt that hydrochloric acid can be made satisfactorily and economically from chlorine, carbon, and water.

(4) *Hydrochloric Acid by Action of Chlorine on an Organic Compound.*

It would appear that the commercial success of processes for the manufacture of hydrochloric acid by the action of chlorine on organic compounds containing hydrogen is dependent on the value of the by-products obtained.

The Bosnische Elektrizitats A.-G. (Ger. P. 158086, of 1905) passes chlorine into retorts, filled with wood and heated to 150° to 300° C. Besides hydrochloric acid, charcoal, tar, acetic acid, and alcohol are recovered. From 100 parts of wood and 15 chlorine, 32 parts hydrochloric acid of 33 per cent. and 30 parts charcoal are obtained.

Aylesworth (U S. P. 914223) passes chlorine through fused naphthalene or other hydrocarbons, thus producing hydrogen chloride and chlorinated naphthalene which may be utilised for impregnating timber.

According to the Consolidierte Alkaliwerke (Ger. P. 313875, of 1918), chlorine acts on lignite without external heating to give hydrochloric acid and chlorinated compounds which may be extracted.

For other patents involving the use of organic materials in the production of hydrochloric acid, see Lasher, Assignor to the Kansas City Refining Co. (U.S. Ps. 1337141; 1300206; 1335743; and 1339519—all of 1920).

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[1] Lorenz, Eng. P. 25073, of 1894; Peter, U.S. P. 1229509, of 1917; Gibbs (*loc. cit.*) states he has U.S. P. pending.

(5) *Simultaneous Production of Hydrochloric and Sulphuric Acids from Chlorine, Steam, and Sulphur Dioxide.*

Masson (Fr. P. 324859, of 1903) obtains hydrochloric acid, together with sulphuric acid, by allowing chlorine and steam to act on sulphur dioxide in a heated space.

The same process has been patented in Britain by Askenasy and Mugdan (B. P. 14342, of 1903), and in Germany by the Consortium fur elektrochemische Industrie (Ger. Ps. 157043 and 157044) The last-named firm allows a mixture of chlorine and SO_2 to meet with water, or, better, hydrochloric acid, flowing down in a reaction-tower; at the bottom sulphuric acid of 65 to 80 per cent runs out and at the top gaseous HCl escapes. It is stated that this process has given satisfactory results in practice, and that it can compete successfully with acids made in the ordinary way According to an investigation by Coppadoro,[1] in working the process the temperature in the apparatus should exceed 70° if 70 per cent. sulphuric acid is to be obtained. Considerable heat is developed in the reaction:—

$$SO_2(\text{gas}) + Cl_2(\text{gas}) + \text{Aq.} = H_2SO_4, \text{Aq.} + 2HCl, \text{Aq.} + 816 \text{ calories.}$$

The reaction requires considerable time and there is some difficulty in freeing the sulphuric acid from HCl. The process is said to be in operation in a works at Ravenna. A great deal of information regarding the process, with estimates of costs, is given by Coppadoro.

Another process for the manufacture of sulphuric and hydrochloric acids simultaneously from chlorine, sulphur dioxide, and steam has been patented by the International Precipitation Co. and H. V. Welsh (U.S. P. 1285856). The sulphuric acid is separated from the gaseous hydrochloric acid by electrical precipitation of the finely-divided suspended particles of sulphuric acid.

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[1] *Gazz. Chim. Ital.*, 1909, **39**, 616.

CHAPTER VII

ABSORPTION OF HYDROCHLORIC ACID

Necessity for Condensation—Injury to Vegetation.

IN the infancy of the sulphate of soda industry, hydrochloric acid was regarded as a useless by-product and no attempt was made to absorb it. So long as the factories were small, the nuisance caused by the escaping acid was tolerated, but as the manufacture increased, municipal intervention became inevitable. It may be of interest to mention that when the Liverpool authorities compelled Muspratt's works to close on account of the nuisance, works were started at Newton Heath, only to meet a similar fate. It was obvious to the manufacturers that some less crude method than shifting factories from place to place must be found; yet it was many years before the problem was satisfactorily solved. In the abstracts of early British patents, is the record of a patent taken out by Mr. Edward Ford on 8th March 1839 which deserves to be remembered by a grateful posterity. His furnaces and factories were to be erected on a ship or flotilla, partly lined with lead, and moored on the high seas sufficiently far from the mainland to prevent injury to vegetation. For this patent the full tax was paid! The patenting of such a proposal may be regarded as an exaggerated expression of the despair with which the problem was regarded.

The first attempt at a remedy was to build enormously tall chimneys, even up to 500 ft., in order to dilute the acid gas with air and smoke, and to discharge at a high level. This proved a complete failure, and in some cases made matters worse, as dense clouds of acid fog descended and laid waste the vegetation for greater distances.

The earliest recorded attempt to absorb the gas by water was made in 1827 at Walker-on-Tyne. The gas was led through flues and chambers into which water was sprayed. Stone towers packed with pebbles or broken glass were also tried, but with very partial success. The first efficient scrubbers were the coke-condensers, which were patented in 1836 by Gossage, and which are still in common use. Strange to say, the absorption in stoneware bottles never appears to have found favour in England at any time although used for over a century on the Continent.

Noxious Effect on Vegetation.—The investigations of the Belgian Commission of 1855 proved conclusively that the dilution of hydrochloric acid with air or smoke is not sufficient to prevent noxious action on vegetation. The second part of their report treats of the influence of wind, barometric pressure, humidity and temperature of the air, topographical situation, configuration of the district, distance from the source of the gas, and other possible factors. An abstract of this report is given.[1] The effect of the gas upon trees and hedges, especially upon their leaves, was investigated with great care. It was found that trees are attacked very unequally, and the following series was established, whose first member, the hornbeam, is most sensitive, whilst the last, the alder, is least sensitive to the gas :—

Hornbeam,
Hazel,
Stone-oak,
Beech,
Birch,
White maple,
Field-maple,
Hawthorn,
Spindle-tree (*Euonymus europæus*),
Elm,
Linden,
Blackthorn (Sloe),
Larch,
Bramble,
Ash,
White poplar,
Italian poplar,
Aspen,
Thuya,
Vine,
Plum-tree,
Apple-tree,
Pear-tree,
Cherry-tree,
Red-currant-bush,
Rose-tree,
Lilac,
Elder,
Raspberry-bush,
Spear-tree (*Spiræa ulmaria*),
Hop,
Alder,
Grey alder.

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[1] *Dingl. polyt. J.*, **165**, 375-427.

The first sign of attack is the appearance of spots on the leaves, and at a more advanced stage the leaves die off. As the buds are better protected, leaves usually appear the next year. Finally, even the buds are attacked and the tree then dies.

Vegetables and crops suffer much less than trees and shrubs. Spots are frequently found on the leaves of potatoes, beans, clover, lucerne, cabbage, turnips, etc., but the plants appear to be little injured, particularly in the case of root-crops. There is considerable divergence of opinion regarding the effect of acid fumes on corn, and the Belgian Commission found no case of damage proved at distances of 150 yards or upwards from the source of pollution. The conflict of evidence on this point is probably connected with the fact mentioned by an Alkali Inspector,[1] that complaints regarding atmospheric pollution are most frequent when crops are bad everywhere.

Alkali-works frequently receive more than their due share of the blame for atmospheric pollution, and in particular are credited with damage done by sulphur dioxide. Dr Angus Smith found the amount of sulphur acids in the atmosphere to be as high as 2518 g. (calculated as SO_3) per million cubic metres of air in Manchester, as against 1760 g. in London and 474 g. in a country district. At the same time, it should be said that there is little doubt that hydrochloric acid is more deleterious in its effect on vegetation than sulphuric fumes.

The injurious effect of acid fumes in the air is probably due mainly to the acids precipitated in solution by rain or dew, rather than to the gases diffused in the air. Damage is rarely observed in dry weather, and becomes quickly noticeable in damp or foggy weather.

Radius of Noxious Effects.—This is naturally largely dependent on the situation of the works, the efficiency of condensation, and many other factors. The Belgian Commission place the minimum at 600 metres (656 yards) and the maximum at 3000 metres (3187 yards). Christel[2] states that effect on vegetation could be proved up to 1000 metres from an alkali-works where efficient condensation appliances were in use. By experiment, he found definite evidence of disturbance of vital functions in plant organs when the air contained 1 part per thousand of hydrochloric acid. According to Dr Angus

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[1] *Annual Report of Alkali Inspectors.* [2] *Wagner's Jahresber.*, 1874, 277.

Smith, if rain contains 10 parts of acid per million, vegetation entirely ceases.

Further investigations on the effect of acid fumes on vegetation will be found in the following:—Sonnenschein, *Dingl. polyt. J.*, 1871, **200**, 336; Hasenclever, *Chem. Ind.*, 1879, 225 and 275; Hamburger, *J. Soc. Chem. Ind.*, 1884, **4**, 202; *Twenty-eighth Annual Report on Alkali Works*, p. 19.

Effect on Human Health.—Many investigations have been made on this subject. Pollution of the atmosphere with hydrochloric acid naturally interferes with the comfort of those living in the district, but there is no evidence of injurious effect on health, except on individuals suffering from chronic diseases of the larynx. No injurious effect has been proved in the case of phthisical or asthmatic complaints. It is stated that the public health statistics of Widnes, one of the greatest centres of alkali manufacture in the world, are more satisfactory than those of any other large city. The Belgian Committee of 1855 found no evidence of injury to health by acid fumes. Reference should be made to the report by Dr Ballard.[1] There are further references in:—*Sixteenth Annual Report on Alkali Works*, 1879, p. 7; *Twenty-ninth Annual Report on Alkali Works*, 1893, p. 26; Jurisch, *Chem. Ind.*, **1903**, pp. 158, 174, 211.

Legislation against Pollution of the Atmosphere.

By 1846, Gossage's coke-towers were universally employed in English works; but, as generally constructed at that time, they were very inefficient; and in consequence of their unsuitable construction and that of the decomposing-pans, furnaces, and conducting-pipes, there were still enormous quantities of uncondensed acid vapours sent into the air. Before 1862, according to an estimate by Fletcher, ten factories in Lancashire alone poured forth weekly 255 tons of dry HCl, and all the English factories together at least 1000 tons. According to Dr A. Smith, the usual loss of HCl in saltcake-making was then 16 per cent. on the average, but 40 per cent. in some cases. In Belgium the Commission of 1855, as can be calculated from their Report (pp. 57 *et seq.*), found even greater losses, viz., in the four factories examined, 43·2, 28·3, 56·9, and 44·4 per cent. of the HCl yielded by the salt. In France Freycinet calculated, in 1866,[1] that at that time one-half of the hydrochloric acid generated went into the air.

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[1] *Eighth Annual Report of the Local Government Board*, Supplement, containing the "Report of the Medical Officer" for 1878, p. 206.

It is not surprising that, under these circumstances, the complaints about nuisance were quite as great as at the time when no hydrochloric acid at all was condensed; for in the meantime alkali-works had increased to such an extent that the absolute quantity of hydrochloric acid escaping uncondensed amounted to much more than that which escaped in the former period, when no condensation at all was attempted. The destruction of the vegetation round the alkali-works was only too evident, without any Commissions of inquiry, although, on the whole, the value of land round the works had increased (Twelfth and Thirteenth Reports, p. 15). It was impossible to ignore the nuisance caused by the smell, and the worse one that iron objects of all kinds, locks, window-fittings, gutters, etc., could not be kept from rusting, that the tools of mechanics were at once blunted, and that even window-curtains were destroyed in a very short time. The public, thus afflicted, can hardly be blamed if they raised the reproach, unjustified as it was, that the alkali-works poisoned the air of the neighbourhood and caused diseases.

The most potent incentive to preventing any waste of products in factories seems always to be the fact that it entails pecuniary loss. But experience has proved in innumerable cases that it does not suffice for preventing such waste: the convenience of many manufacturers, on the one hand, and their employees' insufficient knowledge, on the other hand, have been more than sufficient to counterbalance it. Even the intervention of the courts of law, the claims for damages, and other unpleasantnesses of all kinds could only in isolated cases prevail to bring about a thorough cure. Unfortunately, a pecuniary motive for preventing the escape of hydrochloric acid did not exist; at that time only a small portion of the hydrochloric acid generated in alkali-making could really be brought into the trade as such, or used up in the factories themselves for making bleaching-powder, chlorate of potash, and bicarbonate; of the remainder, all that did not go into the air had, after condensation, to be run into the nearest watercourse, where it killed all the fish and gave rise to fresh complaints.

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[1] *Rapport du Jury International*, 1877, vii., p. 42.

It was inevitable that in the end, resource should be made to legislation to stop the nuisance. In Belgium, this was done in a seemingly thorough and scientific fashion; but in practice it was found that the legislation had failed in its object. Open roasters for calcining saltcake were prohibited and muffle furnaces made compulsory for this purpose. This did not stop the nuisance, because blind roasters (particularly at that time) were anything but trustworthy.

In England, legislative interference with chemical industries has often proved disastrous, but the Alkali Act of 1863 is an outstanding exception to this rule. The Act neither specified nor prohibited any type of apparatus, but made it incumbent on the manufacturer to reduce the escape of hydrochloric acid into the atmosphere to under 5 per cent. of the total hydrochloric acid manufactured. It also established a compulsory registration of all factories manufacturing sodium sulphate and provided for a periodical inspection. Additional Acts in 1874, 1881, and 1906 extended the scope of the original Act so as to apply similar provisions to other processes. The Act of 1874 imposes the further condition that in a cubic foot of the gas escaping from the factory into the atmosphere not more than 0·2 grain of HCl may be present. This is the same as 0·454 g. of HCl per cubic metre, or about three ten-millionths by volume.

An historical survey of the Alkali Acts up to 1892 is given by the Chief Inspector, Mr A. E. Fletcher.[1]

It is stated that just prior to the passing of the first Alkali Act, about one-third of the hydrochloric acid generated went into the atmosphere. By the end of the first year the loss was reduced to 1·28 per cent., in the second to 0·88, and in the third to 0·73. The amount condensed compared with that produced is given in the *Annual Reports on Alkali Works* as follows for recent years:—

Year.	1912.	1913.	1914.	1915.	1916.
Per cent. condensed . .	98·74	98·81	98·49	98·34	97·90
Loss per cent. . . .	1·26	1·19	1·51	1·66	2·10

These figures probably show the loss slightly lower than it actually is, though this may not be the case. The Alkali Inspectors in carrying out their tests aspirate a measured volume of gas from the pipe or flue leading the acid vapours from the furnace and determine the amount of chlorine present. In a similar manner, the chlorine in the exit gas from the condensers is determined and the amount which has escaped condensation thus found. Various minor sources of loss are not measured, but probably these do not amount in total to 1 per cent. of the whole.

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[1] *J. Soc. Chem. Ind.*, 1892, 11, 120.

It has already been mentioned that the Alkali Act is almost a unique exception to the rule that legislative interference with chemical industry in Britain is disastrous. It is only justice to connect this with a tribute to the able manner in which the Alkali Inspectors have done their work.

Theory of the Condensation of Hydrochloric Acid.

The condensation or absorption of hydrochloric acid is comparatively simple from a theoretical point of view, but an extraordinarily large number of papers have been written on the subject, and their authors have vigorously and repeatedly urged their particular views. Much of the controversy has arisen from different understandings of the end in view, and from different opinions as to the best method of attaining one or other of these ends in practice. One party have considered mainly the completeness of absorption of the hydrochloric acid, whilst others were concerned mainly with the practical problem of how to obtain the strongest solution of the acid. Many of the earlier writers appear to have held such peculiar views that their papers have now little but an historical interest, and it is owing mainly to the investigations of F. Hurter, and the exposition and criticism of Hurter's papers by G. Lunge, that the subject is now generally clearly understood. Hurter and Lunge differed on many minor points of theory and detail, but their papers resulted in giving finally a clear picture of the whole subject.

The problem consists in devising the best method of (1) obtaining complete condensation of the hydrochloric acid; (2) obtaining the highest possible concentration of the hydrochloric acid in solution; and (3) effecting these objects with a simple plant which is inexpensive in cost and upkeep.

The problem is complicated by various factors, the most important being variations in the concentration of hydrochloric acid in the gas under treatment, variation in temperature of the original gas, and the difficulties which arise in construction on account of the corrosive nature of both the gas and liquid. An important factor, often overlooked by the earlier investigators, is the large evolution of heat which occurs when hydrochloric acid dissolves in water.

Solubility of Hydrochloric Acid.

The solubility of hydrochloric acid varies with temperature and pressure, but the variations do not conform to the simple laws which are approximately accurate for most gases.

Most of our knowledge of the equilibrium between hydrochloric acid solution, hydrochloric acid gas, and water vapour, is derived from the investigation of Roscoe and Dittmar.[1] Their results are so important for a clear understanding of the conditions for the absorption of hydrochloric acid that a close consideration of them is desirable. Roscoe and Dittmar give their actual experimental figures, and also tables obtained by graphic interpolation. The latter are more convenient for present purposes, and reference may be made to the original paper by those desiring the experimental figures. In some cases in the tables given below, further figures are given. These have been obtained by calculation from the experimental data of Roscoe and Dittmar, except where it is explicitly stated that they are derived from some other source.

Variation of Solubility with Pressure.—The solubility at 0° under various partial pressures of hydrochloric acid is shown in the following table. The pressures given are the partial pressures in cms. of mercury.

Pressure cms	Grams HCl per 1 g. of Water	Percentage of HCl.	Pressure cms.	Grams HCl per 1 g. of Water	Percentage of HCl
6	0·613	38·0	45	0·772	43·4
8	0·640	39·0	50	0·782	43·8
10	0·657	39·6	55	0·791	44·1
12	0·670	40·2	60	0·800	44·4
14	0·681	40·7	65	0·808	44·6
17·5	0·697	41·1	70	0·817	44·9
20	0·707	41·4	75	0·824	45·2
22·5	0·716	41·7	80	0·831	45·4
25	0·724	42·0	90	0·844	45·7
27·5	0·732	42·2	100	0·856	46·0
30	0·738	42·5	110	0·869	46·5
35	0·751	42·8	120	0·882	46·9
40	0·763	43·1	130	0·895	47·2

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[1] *J. Chem. Soc.*, 1860, **12**, 128.

A glance at these figures, or at the curve below, renders it evident that the simple law of Henry is not even approximately true, but that, on the other hand, the amount of gas absorbed increases very little with increase of pressure.

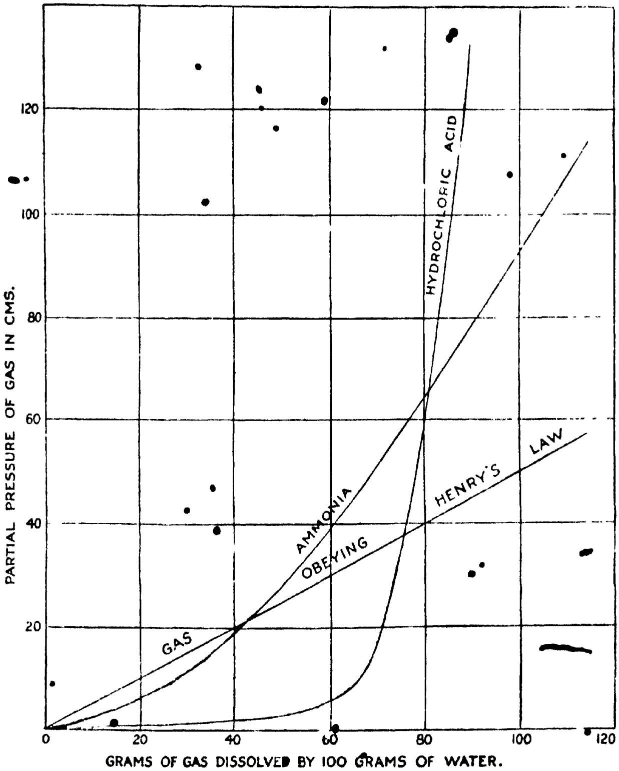

FIG. 66.

According to Henry's law, increase in the partial pressure from 12 to 120 cms. should increase the solubility ten times, yet the amount of hydrochloric acid dissolved by 1 g. of water is increased only from 0·670 to 0·882. For comparison, the solubility curves for a gas which obeys Henry's law and also for ammonia, are shown on the graph.

Variation of Solubility with Temperature.—The table given below is also from Roscoe and Dittmar. The figures are not strictly comparable, since the partial pressures of HCl are different at every temperature. The solubilities were measured in each case at a *total* pressure of 760 mm., made up of the partial pressures of hydrochloric acid and water vapour. In the preceding section it was shown that the solubility is influenced far less than is usual for gases by the pressure; consequently these figures give a rough approximation to the values with a constant partial pressure of hydrochloric acid at various temperatures.

Temp. °C	HCl grams dissolved by 1 g. of Water.	Per cent. HCl in Solution	Temp. °C	HCl grams dissolved by 1 g. of Water.	Per cent. HCl in Solution.
0	0·825	45·2	48	0·603	37·6
4	0·804	44·6	52	0·589	37·0
8	0·783	43·9	56	0·575	36·5
12	0·762	43·2	60	0·561	36·0
16	0·742	42·6	...	...	...
20	0·721	41·9	...	...	...
24	0·700	41·2	...	.	...
28	0·682	40·5	...	..	..
32	0·665	39·9	110	...	20·24
36	0·649	39·4			
40	0·633	38·8			
44	0·618	38·2			

Apart from the measurements of partial pressures of solutions at 0° by Roscoe and Dittmar, a few measurements at 25° by Gahl[1] are available. The best series of measurements for our present purpose are those by Dolezalek at 30°, which are given in the following table. The first and last columns are calculated from Dolezalek's data, as they show up the great practical importance of these determinations.

A study of the figures on p. 235 leads to conclusions which, in view of much that has been written on the absorption of HCl, are certainly of great interest. To take one example:—A gas which contains only 1 per cent. of HCl can theoretically yield a 27 per cent. solution of hydrochloric acid, whilst a gas containing little over 2 per cent. of HCl can theoretically give a 30·0 per cent. solution, assuming in both cases that gas and solution can be cooled to 30° and brought thoroughly into contact before the liquid is removed.

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[1] *Z. physik. Chem.*, 1900, **33**, 178.

Table calculated from Data of Dolezalek,[1] *showing Percentage of HCl in Solution at 30° obtainable with Various Concentrations (Partial Pressures) of HCl Gas.*

Per cent. HCl by Volume in Gas at 760 mm. Total Pressure.	Corresponding Partial Pressure of HCl mm.	Grams of HCl per 100 g. Water.	Percentage of HCl obtainable in Solution
0·031	0·24	20·1	16·7
0·049	0·37	22·5	18·3
0·068	0·52	24·8	19·9
0·091	0·69	26·8	21·2
0·093	0·71	27·1	21·3
0·126	0·96	29·6	22·8
0·175	1·33	32·2	24·4
0·186	1·41	32·7	24·6
0·435	3·34	34·1	25·4
0·53	4·10	34·9	25·9
1·02	7·75	37·3	27·2
1·47	11·20	40·1	28·6
1·67	12·74	41·2	29·2
2·04	15·5	42·8	30·0
4·15	31·5	45·7	31·4
7·3	45·5	47·3	32·1
8·7	66·0	48·6	32·7
14·7	112	51·8	34·2
17·6	134	53·0	34·7
22·4	170	54·8	35·4
24·8	189	55·7	35·8
36·4	277	58·2	36·8
41·2	313	59·1	37·2
44·3	337	59·9	37·5

In view of the definite statements made as to the alleged impossibility of obtaining anything like these results in practice, it may be well to emphasise the fact that such results are possible, and in fact must be obtained, if (1) the gas and liquor are cooled to the temperature stated; and (2) the gas and liquid are intimately mixed for a definite small period of time.

The great importance of temperature may be demonstrated by a comparison of the equilibrium figures at 0° (from Roscoe and Dittmar's data) and at 30° (from Dolezalek's data).

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[1] *Z. physik. Chem.*, 1898, **26**, 334.

The extraordinary influence of temperature is well shown by the fact that at 0° a solution containing 37·5 per cent. of HCl is obtainable with a gas containing only 7 per cent. of HCl, whereas at 30° such a concentrated solution is only obtainable if the gas contains 45 per cent. by volume of hydrochloric acid.

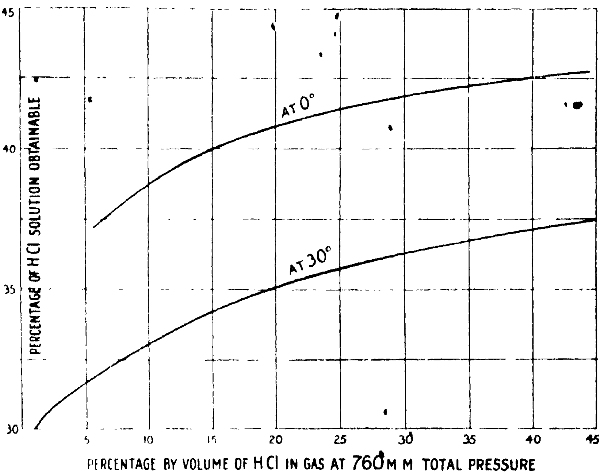

FIG. 66 A.

Heat Evolution during Condensation.

From the figures showing the variation of solubility of hydrochloric acid with pressure and temperature, it will be seen that the variation from the laws for an ideal gas are very marked. These variations must be clearly understood for an understanding of the condensation problem, but they require to be considered in conjunction with what is perhaps the most important factor of all, the enormous heat evolution which occurs during condensation.

It may be well to consider from the theoretical point of view the various factors influencing the heat evolution during condensation, though these can not be dealt with separately when the practical problem is considered. The principal heat factors are:—

(a) *Specific heat of steam.*
(b) *Specific heat of hydrochloric acid gas.*
(c) *Heat of condensation of steam.*
(d) *Heat of solution of hydrochloric acid.*
(e) *Heat of dilution of hydrochloric acid solution.*
(f) *Specific heat of hydrochloric acid solution.*

The heat evolution which occurs during condensation is due to the sum of these effects. The relative importance of the individual factors will be indicated by the following data.

Specific Heat of Steam.—The following data are available for the specific heat at constant pressure:—

Temperature.	Specific Heat.	Observer.
100°	0·421	Thiesen
180°	0·51	"
100-125°	0·3787	Gray
128-217°	0·4308	Regnault

Specific Heat of Hydrochloric Acid Gas.—The following figures are for the specific heat at constant pressure:—

Temperature.	Specific Heat.	Observer.
13-100°	0·1940	Strecker
22-214°	0·1867	Regnault

It will be noticed that the specific heat of steam is about two and a half times that of hydrochloric acid, and that, even apart from the large effect due to its high latent heat, the presence of steam will add greatly to the work of the condensers. The high specific heat of steam suggests, *a priori*, that the introduction of superheated steam into the furnace (Wigg, B. P. 5105, of 1879) would cause trouble in the condensation process, and it is not surprising that this was not a success.

Heat of Condensation of Steam.—The latent heat of evaporation of water is 534 calories per gram at 100°, and does not vary much over the range of temperature with which we are concerned, as the actual condensation will always take place in the neighbourhood of 100°.

Heat of Solution and Dilution.—The following figures are from *Landolt-Börnstein's Tabellen*, and show the heat evolution when 1 gram-mol. of hydrochloric acid is dissolved in n gram-mols. of water.

$n =$	1	5	10	50	100	300
	53,700	14,960	16,160	17,100	17,200	17,300

From these data Thomsen[1] shows that the thermal effect can be expressed by the equation

$$(\mathrm{HCl}\ (m+1)\ \mathrm{H_2O}) = \frac{m}{m+1} \cdot 11980 + 5375 \text{ calories,}$$

where m is the number of gram-mols. of HCl.

The extreme cases are of interest. For $m = 0$, and $n =$ [illegible],

$$(\mathrm{HCl}, \mathrm{H_2O}) = 5375 \text{ calories,}$$

which is the thermal effect due to the absorption of 1 gram-mol. of HCl in 1 gram-mol. of H_2O.

When $m = \infty$,

$$(\mathrm{HCl}, Aq) = 17{,}355 \text{ calories,}$$

which is the *maximum* heat of absorption for a gram-mol. of HCl in water.

It will be noticed that there is a very marked heat evolution on solution. The heat evolution when 1 g. of HCl is dissolved in sufficient water to give a 30 per cent. solution is about 400 calories.

Specific Heat of Hydrochloric Acid Solution.—In Miss Burke's translation of Thomsen's *Thermochemistry*, p. 161, the specific heats for solutions of hydrochloric acid are given as follows:—

$n =$	10	20	50	100	200
Sp. Heat =	0·749	0·855	0·932	0·964	0·979

where $n =$ the number of gram-mols. of water per gram-mol. of HCl. The specific heat of a hydrochloric acid solution is evidently always lower, though of the same order of magnitude as that of water.

Relative Influence of Various Factors on Thermal Effect in the Condensation of Hydrochloric Acid.—With the above data we are in a position to compare the relative importance of the various heat changes which occur when hydrochloric acid solution is obtained from a hot gaseous mixture containing acid and steam.

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[1] *Thermochemische Untersuchungen*, vol. iii., pp. 11 and 71.

Cooling 1 g. of steam from 500° to 100° . .	about	200	calories
„ 1 g. of water from gas to liquid . .	„	530	„
„ 1 g. of HCl from 500° to 100° . . .	„	70	„
Solution of 1 g. of HCl to give 30 per cent. solution	„	400	„
Cooling of 1 g. solution from 100° to 30° . .	„	75-100	„

It is more instructive to compare the heat changes which will occur with mixtures of acid and water approximating to those found in technical practice.

When 142° Tw. sulphuric acid is used with absolutely dry salt, 38 parts of water are evolved for each 100 parts of anhydrous HCl In practice the proportion of water will be raised by moisture from the salt, and even more so, in the case of open roasters, by water formed during combustion. This may be taken then as the absolute minimum of water likely to be present. Taking as a unit quantity 1 g. of HCl, we will have with it 0·38 g. of water. The relative importance of the various heat factors will be seen from the following table:—

Cooling 0·38 g. of steam from 500° to 100° . .	about	76	calories
„ 0·38 g. of water from gas to liquid . .	„	200	„
„ 1 g. of HCl from 500° to 100° . .	„	70	„
Solution of 1 g. of HCl to give 30 per cent. solution (assuming extra water required to be added as cold water)	„	400	„
Cooling of 3 g. of solution from 100° to 30° . .	„	270	„
Total heat change . .	„	1016	„

With 126° Tw. sulphuric acid and dry salt, each 100 parts of HCl would be accompanied by at least 55 parts of water. Making a moderate allowance for water from dampness of the salt, combustion of fuel, etc., we may easily have 70 parts of water per 100 of HCl. Assuming, then, that each gram of HCl has with it 0·70 g. of water, the heat change will be made up approximately as follows:—

Cooling 0·70 g. of steam from 500° to 100° . .	about	140	calories
„ 0·70 g. of water from steam to liquid .	„	370	„
„ 1 g. of HCl from 500° to 100° . . .	„	70	„
Solution of 1 g. of HCl to give 30 per cent. solution (assuming extra water to be added as cold water)	„	400	„
Cooling 3 g. of solution from 100° to 30° . .	„	270	„
Total heat change . .	„	1250	„

In the above analysis of the factors involved in the heat change which accompanies condensation, certain simplifications and assumptions have been made in order to confine attention to the main factors. The only omission which has a sufficiently large influence to affect appreciably deductions drawn from these data is the effect of the heated air drawn with the vapours from the pan to the condenser. The amount of this air varies so largely between open and muffle furnaces, and even between furnaces of identical type, that it is difficult to give, even an approximate value to its effect. This factor must, however, be kept in mind when considering these figures. It is never likely to be below 25 per cent. of the total cooling required, and may with very dilute gases run up to over 90 per cent. of the total.

Cooling Gas before Liquid Condenses.—In the two cases, considered on p. 239, this represents 14 and 17 per cent. of the total heat change. As, however, these gases will be mixed with at least an equal volume, and possibly even ten times their volume of air which must also be cooled, this is an underestimate of the work to be done in cooling the gases. According to the dilution of the hydrochloric acid, this may represent from 20 to 80 per cent. of the total cooling work to be done.

Condensing Water Vapour.—The amount of water present obviously has a large effect on the heat evolution. In the two cases examined, the extra water introduced through using 71 per cent. sulphuric acid instead of 78 per cent. sulphuric acid increases the cooling work to be done by 25 per cent. (This ratio will be reduced and become, therefore, of somewhat less relative importance when much air is present.)

Heat of Solution.—In normal practice, where a concentrated acid is desired, solution cannot be completed until the liquid is cooled to a low temperature. The amount of heat given out is so great that if no heat is withdrawn cold HCl passed into cold water will reach the boiling point by the time sufficient HCl has dissolved to give a 20 per cent. solution.

The Cooling Problem.

From a study of the partial pressure data, it is evident that it is possible to obtain strong acid even with dilute gases if two conditions can be filled, namely:—

(*a*) Sufficient cooling to remove not only the heat of the gases but the heat of solution; and

(*b*) Sufficient contact surface and time to allow equilibrium to be reached.

The second problem will be treated in the next section, although practically it is impossible to separate its consideration from the problem of cooling. The old coke-tower, for example, might be excellent as a scrubber, but its thick walls render it about the worst possible arrangement for cooling purposes.

If water-jacketed metallic coolers could be used the problem would be comparatively simple, but unfortunately this is impossible. Provided, however, that no liquid is condensed, cast-iron is practically unattacked, and the gas should therefore be cooled to as near 100° as possible, without allowing any condensation. In practice, this is best done by finding by trial the maximum length of iron flue which can be inserted between the furnaces and the condensers. Particularly in the case of dilute gases is pre-cooling in iron pipes advantageous; in some cases about 80 per cent. of the total cooling work may be done by the cast-iron pre-cooler. In large installations a further cooling in porcelain or glass pipes should occur before the condensers or towers are reached.

A liquid is much easier to cool than a gas, and the rational method of cooling is to pass cold liquid down the tower against the gas current, withdraw the liquid, cool it thoroughly, and use it for cooling more gas. A series of scrubbers with the liquid passing "counter-current" against the gas current, and thoroughly efficient, repeated cooling of the liquid, appears the only rational alternative to the old way of making towers "big enough."

The Absorption Problem.

The chief factor for good absorption is the area of gas-liquid interface offered per unit volume of gas per unit of time. Hurter discussed in his various papers how to obtain the maximum contact-time efficiency, and considered the relative advantages of tower packing, bubbling gas through liquid, and spraying the liquid through gas. Hurter's pioneering work is discussed and criticised fully by Lunge (see last edition of this book, Vol. ii., Part I.), and proved of great practical value. Hurter's papers will be found in the *J. Soc. Chem. Ind.*, 1885, 639; 1887, 707; 1889, 861; 1893, 227 and 989. For criticisms, see Lunge,[1] and in last edition of this book. Hurter concludes that the best form of condensing apparatus is the coke-tower, and entirely condemns the spraying plan both in theory and practice. His main objection, that it is impossible to obtain the same surface or time of contact between gas and liquid as in bubbling gas through liquid, has been adversely criticised by Lunge, and is certainly of very doubtful validity.

For some time after these papers by Hurter and Lunge, little was published beyond recommendations of various shapes of tower packings.

Meyer[2] has a thoughtful discussion of the condensation problem.

Partington and Parker[3] in connection with the absorption of nitrous fumes consider the theory of gas-absorption in packed towers, and take account of the fact that the dissolution of a gas in a liquid is not an instantaneous process. Donnan and Masson[4] discuss the general theory of gas-absorption in packed towers. For purposes of simplicity in the mathematical treatment, they have made several simplifying assumptions, such as constancy of temperature, which prevent the direct application of their results to the present problem. Their initial survey of the problem shows in a quantitative manner that high absorption efficiency depends on :—

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[1] *Z. angew. Chem.*, 1893, 328.

[2] *Z. angew. Chem.*, 1913, **26**, 97.

[3] *J. Soc. Chem. Ind.*, 1919, 75.

[4] *J. Soc. Chem. Ind.*, 1920, **39**, 236.

(*a*) High interfacial area between gas and liquid.
(*b*) High relative motion of gas and liquid.
(*c*) High degree of turbulent motion in one or both phases.
(*d*) Sufficient rate of flooding to secure a maximum drip effect.

Before proceeding to a description of the plant, a synopsis of the views of various authorities may be given.

Dr Angus Smith advocated the strongest possible cooling of the gas before exposing it to the condensing action of the water.

Dr Lunge advises: "Do not cool the gas too much at first, but allow it in the hot state to meet so much water that this is mainly vapourised, and then expose the mixture to the utmost possible cooling on its further progress." "The best plan for uniting complete condensation with the production of the strongest acid seems to be a combination of receivers or cisterns and coke-towers or plate-towers."

Dr Ferdinand Hurter regarded the coke-tower as undoubtedly the best form of condenser. A special advantage of the coke-tower is that it retains so much liquid that it renders harmless minor inequalities in working.

T. Meyer (*loc. cit.*) advocates for a complete absorbing system the following (*a*) one or two water-jacketed coolers without added liquor inside, simply for cooling and to condense sulphuric acid, etc.; (*b*) a stoneware fan giving the minimum draught with which the plant can be operated; (*c*) a gas-filter filled with granulated acid-proof material; (*d*) a series (or several series in parallel) of water-cooled Cellarius absorbers; and finally (*e*) a small cylindrical stoneware tower in which the gases are scrubbed by atomisers delivering spray.

Modern practice in general follows the lines of Meyer's scheme. The use of glass coolers and cooled absorbers, followed by packed towers or smaller coke-towers is steadily extending. In modern plants great attention is paid both in design and working to obtaining the minimum adequate draught.

Progress of the Evolution of Gas and Temperatures.

The following statements on the progress of the evolution of HCl in the manufacture of saltcake and on the temperature of the gases refer to some operations carried out at the Griesheim Chemical Works, under the management of Mr Stroof. They are given here as typical for normal work, but they require for their proper appreciation a previous description of the apparatus employed.

Some of the saltcake furnaces (set A) are provided with stone cisterns for the pan-gases, others (set B) with stoneware receivers (Woulfe's bottles). In set A the gases of two pans, working with a common roaster, first pass singly into a stone cistern, then altogether through a set of stoneware pipes, through twelve stone cisterns and into a stone tower 100 ft. high. The cisterns have a width of 6×6 ft. inside – that is, a horizontal surface of 3·24 sq. metres or altogether 38·88 sq. metres. In set B each pan is connected with a stone cistern; then comes a large Woulfe's bottle, from which start two rows of such bottles, eleven in each row, connected by elbow-pipes 3 ft. 3 in. high (see below). The two sets unite in another large jar, and the gases from two such double sets again coalesce in a receiver connected with the stone tower. The two pans thus possess forty-nine stoneware bottles, of a total horizontal area (at the level of acid) = 21·56 sq. metres. All the pans from six furnaces ultimately work into the same stone tower.—The roaster-gas passes first through a cast-iron pipe, then through stone channels, and at last through stoneware pipes into a tower, one tower serving for three roasters.—The observations of temperature and the composition of the gases (per cent. by volume) during some working periods showed the following results:[1]—

Set A. *Condensation by Stone Cisterns.*

In four hours 14 cwt. of rock-salt (98 per cent. NaCl) was charged, corresponding to 416·3 kg. HCl = 254·5 cbm. at 0° and 760 mm. The operation began at 2.30 P.M.

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[1] Unfortunately it is not stated at what stage the observations were made; in the case of the pan-sets they were no doubt taken shortly before the gas entered the stoneware receivers; in the case of the roaster sets, probably after cooling by the iron and stone conduits. This uncertainty can only influence the temperatures.

Pan set.				Roaster set.			
Time.	Temp.	Volume per cent HCl.	Volume per cent. Oxygen.	Time.	Temp	Volume per cent HCl	Volume per cent. Oxygen.
	Degrees				Degrees.		
2.30	80	8·4	18·6	2.30	188	1·0	21·0
2.45	75	18·2	16·8	2.45	188	1·0	20·8
3	70	2·8	20·7	3	188	1·6	20·8
3.15	67	1·8	20·4	3.15	188	1·0	20·8
3.30	70	29·8	14·2	3.30	195	2·0	20·4
3.45	71	21·2	16·8	3.45	198	1·4	20·6
4	70	15·8	17·0	4	196	1·4	21·0
4.15	66	16·4	17·0	4.15	196	0·4	20·6
4.30	74	23·8	15·4	4.30	196	0·8	20·8
4.45	72	22·2	16·0	4.45	194	1·0	21·0
5	76	2·6	20·4	5	194	1·4	20·4
5.15	82	8·2	18·8	5.15	193	1·0	21·0
5.30	78	4·4	20·0	5.30	194	1·6	20·8
5.45	73	11·4	18·0	5.45	200	1·4	21·0
6	67	4·6	19·8	6	198	1·4	20·6
6.15	72	6·2	19·4	6.15	197	1·6	20·6
6.30	85	7·6	19·0	6.30	195	1·4	20·6
Average	...	11·73	18·07	Average	...	1·26	20·75

We will now utilise these observations for making a calculation of the composition and quantity of the gases passing through the apparatus. If we assume that of the 254·5 cbm. HCl (calculated at 0°) two-thirds have been given off in the pan and one-third in the roaster, we have for the pan :—

169·7 cbm. HCl at 0°
= 216·3 „ „ 75°
1586·2 „ air at 75°
1802·5 „ gases given off in four hours ;

or, per second,
0·015 cbm. HCl
0·110 „ air
0·125 „ gases.

In the case of the roaster :—

84·8 cbm. HCl at 0°
= 147·0 „ „ 200°
11520 „ air at 200°
11667 „ gases in four hours ;

and, per second,
0·01 cbm. HCl
0·80 „ air
0·81 „ gases.

Set B. *Woulfe's Bottles* (one analysed).

In three and a half hours 14 cwt. of rock-salt decomposed 7 cwt. per pan. Observations made every quarter of an hour.

Pan set.			Roaster set.		
Temp.	Volume per cent. HCl	Volume per cent Oxygen	Temp	Volume per cent. HCl	Volume per cent. Oxygen.
Degrees			Degrees.		
80	29·6	14·4	256	4·2	20·2
97	22·0	14·4	242	3·2	20·2
97	23·2	14·8	242	2·2	20·2
92	5·0	19·8	256	1·4	20·4
88	6·0	19·8	254	1·4	20·4
82	1·2	20·6	260	1·4	20·6
72	8·8	19·2	258	2·4	20·4
70	33·4	13·8	248	1·8	20·0
66	55·4	9·2	248	2·6	20·4
76	85·4	2·8	254	2·0	20·4
76	75·4	5·0	258	1 8	20·4
70	60·0	8·0	268	4·0	20·0
76	25·6	14·8	244	3·6	20·0
76	26·4	15·6	252	4·4	19·6
86	15·4	17·0	244	3·2	19·8
Average	31·8	14·0	Average	2·64	20·2

If we divide the gas, as before, between the pans and roaster, we obtain for the pan:—

109·7 cbm. HCl of 80°
235·3 „ air „ 80°
345·0 „ gases in all,

or, per second,
0·0085 cbm. HCl
0·0185 „ air,
0·0270 „ gases.

For the roaster (served by two pans):

162·5 cbm. HCl of 250°
5992·8 „ air „ 250°
6155·3 „ gases in all;

or, per second,
0·013 cbm. HCl
0·475 „ air
0·488 „ gases.

In considering these figures we must take into account that in set A (stone cisterns) the united gases of both pans belonging to a furnace were analysed, but in set B (stoneware receivers) only the gases from one pan; by means of the oxygen determination the volume of air mixed with the HCl gas could be estimated. As there are always six charges made in twelve hours, the analyses show the progress of the operations. We perceive in the first instance that even at the same works, with identical (first class) management, very great differences occur in the composition of the gases. In set A, where both pans combine their gas in the first cistern, the average is only 11·73 per cent. HCl, against 31·8 per cent. in set B; evidently in A the pan-doors had been more frequently opened, and there must have been more in-draught even with closed doors then in set B.

The analyses show most clearly that directly after charging a large quantity of HCl is evolved, up to 85 per cent. of the gases; towards the end of the operation this diminishes to a few per cent. It is most remarkable that in spite of the strong dilution of the pan-gas in the cistern-set A, the condensation in the troughs is much better than in the stoneware bottles B—that is, much more uncondensed HCl gets into the tower from the latter, although the cooling must be very good in the long pipes connecting the receivers (altogether about 300 ft. long), and although the thin walls of the bottles must conduct the heat away much better than the stone cisterns. This is evidently caused by the fact that the total absorbing surface of the cisterns is 38·8 sq. metres, against only 21·56 sq. metres, of the bottles. The temperatures in both cases are about the same. This once more proves the great importance of extended surface contact.

It is striking how poor the muffle-gases were. They contained at most 4 per cent. HCl and went down to 0·4 per cent. Here also one of the furnaces yielded gas twice as rich as the other.

Th. Meyer[1] states the percentage of saltcake-furnaces as follows:—

Furnace with two pans	29·8 to 1·8,	average 11·7	% HCl by vol. in	pan-gases.
” ”	2·0 ” 0·4,	” 1·3	” ”	muffle-gases.
Furnace with one pan	85·4 ” 1·2,	” 31·8	” ”	pan-gases.
” ”	4·4 ” 1·4,	” 2·6	” ”	muffle-gases.

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[1] *Fabrikation von Sulfat und Sulzsaure*, p. 35.

Apparatus for condensing Hydrochloric Acid.

The task of condensing the hydrochloric acid is different, according to whether the whole or most of the acid is to be brought to saleable strength, or only sufficiently concentrated for own use, or merely to prevent the escape of any HCl into the air, without any regard to the strength of the condensed acid, the latter being partly or entirely run to waste. The last case will hardly ever happen now; the first case is still exceptional in England, but pretty frequent on the Continent; the second case, where the condensed hydrochloric acid is almost or quite all used up at the works, is the most frequent one in the large centres of alkali-making. The condensing-appliances must necessarily be chosen differently, according to whether one or the other of the above cases has to be provided for; and this difference must begin with the choice of the apparatus for decomposing the salt itself.

If the task is that of bringing all condensed acid to 32° or 36° Tw., none but blind roasters can be employed, and, in condensing, either stoneware receivers or cisterns must be added to the towers, so that not only the pan-acid, but also the roaster-acid can be made strong enough. If one-third of the acid corresponding to the yield of the roaster can be used up at the works, open roasters may be employed, if fired with coke; with proper appliances they furnish acid of 22° to 26° Tw., which is still suitable for chlorine-making. If the roaster-acid is not wanted at all, or only in the state of weak acid (for instance, for bicarbonate), the open roasters may even be fired with coal; but then the condensers must be packed very loosely with bricks, so as not to be stopped up by soot, and the condensed acid will only show from 3° to 6° Tw. The condensation of the two-thirds of acid escaping from the pan will of course take place exactly as in the first case.

With open driers, separate condensing-apparatus must always be provided for the pan and the furnace; from the pan, equally strong acid is obtained as by any other process; from the furnace, even when firing with coke, rarely anything above 22° to 24° Tw., frequently less than that; and whilst the pan condensers may be in direct communication with the air, of course the roaster condenser, through which all the fire-gases pass as well, must be connected with a chimney.

In the case of blind roasters it is an open question whether it is preferable to employ special pipes, condensers, etc., for pan and roaster, or not. Frequently both currents of gas are united and sent into the same tower. This, however, does not seem to be the best plan. The pan-gas is much more concentrated than the muffle-gas, as we have seen, pp 245 and 247, since during the turning over of the charge a good deal of air is carried through the open working-doors into the muffle; and in any case the latter gives off much less gas in the same time and for the same cubical space than the pan. Moreover, the pan-gas is much cooler and more easily condensed For these reasons, the pan-gas is more easily dealt with than the roaster-gas, and it does not seem rational to mix them, instead of erecting special condensing-apparatus for each:—simple fireclay or glass pipes and tightly packed condensers, open at the top, for the pans; and, on the other hand, longer and wider cooling-flues, partly of metal, partly of stone or fireclay pipes (preferable to brick flues), along with more widely packed condensers, connected with the chimney, for the roasters. The latter is recommended because the roaster requires a stronger draught to prevent the gas from blowing out of the working-doors. In case of need the same coke-condenser can be used for both gases, after the roaster-gas has been cooled down to the temperature of the pan-gas; but even then one advantage is sacrificed which the separation of the gases affords and which in some cases is very valuable, viz., collecting the purer pan-gas, nearly free from sulphuric acid, separately from the much less pure roaster-gas. We will cite some special instances.

At St Rollox the arrangement was found by E. Kopp, as follows (the works of Messrs Tennant at Hebburn-on-Tyne possessed open roasters, and consequently a totally different condensing-plant):—viz., the pan-gas travels through a stoneware pipe 15 in. wide, first 17 ft. upwards and then, descending gradually to the condenser, a length of 125 ft. The gas of the roaster (the furnace is 15 ft. wide and 30 ft. long outside) travels through a pipe of 12 in. diameter the same way as the pan-gas, and into the same condenser; but the two gases are mixed only inside the latter. Each condenser is 6 ft. square by 46 ft. high, apart from a foundation of 6 ft. and the house for water-cisterns, etc.

At Messrs Chance's, at Oldbury, the gases were likewise mixed in the condensers, of which there were always two combined, so that the gases ascend one and descend the other (this is not a good arrangement); at last they passed through a small chamber, which could be entered by a man in order to satisfy himself of the progress of condensation. Each tower was 3 ft. 3 in. square, and had a working height of 36 ft. Both those plants (which have been probably altered since) would nowadays be called partly obsolete.

At one of the best-managed works in Widnes, the gases from plus-pressure furnaces were first conducted into stoneware pipes, 150 ft. long, then into a series of stone cisterns, and at last into stone coke-towers, 7 × 7 × 50 ft. The gas of two pans and furnaces combine in the last stone cistern before entering the coke-towers. For each two sets—that is, for four saltcake-furnaces—there is a post-condenser of the same size; but owing to the very careful coke-packing of the principal towers there is hardly any work for the post-condensers, the acid from which runs off only 1° Tw. The same works possessed a Hargreaves plant, the gas from which was cooled by a long set of stoneware pipes down to 38°; it was then taken through two coke-towers, 7 × 7 × 50 ft., one of which serves as post-condenser.

At Chauny the gases from the Mactear furnaces (fired with coke) are treated as follows:—They go first into an octagonal stone tower, serving for a first cooling and for catching the dust, then through wrought-iron pipes, and further on through stoneware pipes, then into a stone cistern divided into two compartments by a partition, in which they are made to pass from one compartment into another by a number of tall elbow-pipes, which effect a thorough cooling. Then comes the principal octagonal coke-tower, made of stone-slabs: this is fed by the weak acid from a wooden post-condenser, pumped up by means of an ebonite pump and stored on the top by means of a number of stoneware bottles, connected so as to form a single reservoir. Even by means of this complicated arrangement the acid never exceeds 28° Tw., which must be considered a maximum for Mactear furnaces.

The Griesheim condensing-plant has been described, p. 244.

It seems more rational, if several decomposing-furnaces are present, to restrict the number of condensing-towers by conducting the gas of two or even more pans into one, and that of the corresponding roasters into another. Of course the condensers must be made larger, in proportion to the larger volume of gas; but in this way the condensers are more evenly worked than if each pan has its own tower. In the latter case, shortly after charging the pan much more acid vapour will rush into the tower than later on. Properly speaking, at the beginning much more water ought to be run down the condenser than afterwards; but this is not practicable, on account of the great trouble it would give. If, however, the gases from two pans go into the same condenser, their charges will be so timed that, with hourly charges, the gas from one pan will always come half an hour after that from the other; the principal evolution of gas in the first pan will be already over when it begins in the second, and so on. Thus there will be a much more uniform mixture of gases in the condenser. There will also be a considerable saving of condensing-space, as the condensing plant required will obviously be less if the maximum from one pan coincides with the minimum from the other.

It is true that the above-mentioned interval of half an hour is not always easily adhered to; for since the pan-men have to wait for the roaster-men getting their charge finished, and the latter cannot always finish in time, disputes frequently arise between them, and the men have to be carefully looked after in this respect. The proposal of Kopp, to group *four* pans together, which would have to be charged at regular intervals of fifteen minutes each, is altogether impracticable for the same reason. When the pans are not charged hourly, but at longer intervals, a regular rotation between them is much more easily carried out.

Instead of two or more pans or close roasters a common condenser is occasionally met with for two or more open roasters: in this case the evolution of gas is far more regular, especially since the proportion of acid vapour in the fire-gas is comparatively small.

In the case of stoneware receivers there are always separate strings of bottles for each pan and for each roaster.

Cooling the Gases. Conducting-pipes.

We have already seen that, according to the almost universal opinion, the gases should be well cooled before they are introduced into the coke-towers, receivers, and so forth. The more the gases are previously cooled, the less work the condensers have to do, and condensation is all the more perfect. In a rational condensing-apparatus the gas must always pass through a channel where it can be cooled by the outer air; this is best done by pipes of different material, either by themselves or in connection with stone tanks offering a large surface. In some places there are large brick chambers (not filled with coke) for the same purpose. The stoneware receivers, if employed in this way—that is, in connection with a coke-tower—also act very well indeed.

The most suitable occasion for cooling by pipes is when the decomposing-furnaces are at some distance from the condensers; sometimes they are purposely laid out in this way up to 300 ft. away from the towers; or, if the space does not admit of a long horizontal conduit, the gas is sometimes first taken upwards, say 50 ft., and then downwards again, before entering the condensers. (*Cf.* later on.)

Some direct experiments on the cooling action of earthenware pipes are described in the *Third Report on the Alkali Act*, p. 40. At Kurtz's works, at St Helens, the pan- and furnace-gas together pass through a 12-in. pipe. Just behind the furnace the temperature was 170° C.; 6 ft. 3 in. further on, 136½°; and 7 ft. 3 in. further on, 110° C.; thus in a length of 13 ft. 6 in. it had been lowered by 60° C.—that is, 4·44° C. per foot of its course. Now the gas entered into a stone tank of a capacity of 200 cub. ft., and left it with a temperature of 76·5°; after a further passage through 18 ft. of 12-in. pipe its temperature was 60° C.; the condensation in the coke-tower was perfect. It is true that the outer temperature during the experiment was only 6° C.

At another works the temperature of the gas after passing through 94 ft. of earthenware pipe sank from 162° to 75½° C.; and after the first 40 ft. it had got down to 86·5°. In a third works, also perfectly condensing its HCl, the gas just behind the pan showed 123° to 149°, and after passing through 250 ft. of piping, 34° to 41° C.

Very instructive are some observations on the cooling influence of different kinds of gas-flues contained in the Fourth Report, p. 53. All three flues belonged to open roasters. The first was an *underground brick flue*, 160 ft. long, of 1600 cub. ft. cooling-space. Temperature on entering, about 360°; on leaving, 300° C.—that is, a cooling of nearly 4° C. for each 10 ft. length, or of 10° C. for each 261 cub. ft. The second was an *overhead brick flue* 160 ft. long and containing 1300 cub. ft. cooling-space. Temperature on entering, 360° C.; on leaving, 88° C.; cooling 17° C for each 10 ft. length, or 10° C. for each 47·7 cub ft. The third consisted of *cast-iron pipes*, 2 ft. 3 in. wide and 130 ft. long, of a capacity of 518 cub. ft. Temperature on entering, 360°; on leaving, 138° C.; cooling about 17·1° C. for each 10 ft. length, or 10° C. for each 23·2 cub. ft. In later Reports we find the following statement for cast-iron pipes:—length of piping 124 ft., cooling from about 360° C. to 138° C.; length of piping 105 ft., cooling from 470° (pyrometrical measurement) to 138° C. *Glass* pipes, which can hardly compete with the materials just mentioned, will be spoken of later on.

A proposal for further cooling the gas, made by J. Mather, is communicated by Dr A. Smith, who himself was not very hopeful about it. Air is to be compressed, cooled down to the ordinary temperature, and introduced into the gas, which it is to cool on expanding. It is well known that the generation of cold by the expansion of previously compressed and cooled air is not at all a cheap process; and in this case the condensation is certainly rendered as much more difficult by dilution with air as it has been aided by cooling. A sketch of his apparatus is found in the *Eleventh Report on the Alkali Act*, p. 39.

The conducting-pipes for the gas were formerly always made of a tapering shape, one pipe projecting into another, with the cement stemmed in between them (see Fig. 67). The amount of the tapering is such that pipes of 4 ft. 6 in length are 15 in. wide at one end and 18 in. at the other. Such pipes can only be made by hand, and are consequently dear. Many manufacturers therefore choose the shape Fig. 68, which is much more easily and cheaply made. The joints are made good by the above-described tar and china-clay cement. Linseed oil and red lead is also sometimes employed, but it is much dearer and not so suitable.

As far as the size of the pipes is concerned, a 15-in. pipe will do for both pan- and roaster-gas of a blind roaster producing 40 tons per week. Some factories only make them 12 in. wide; but 15 in. is preferable, on account of taking the gas away more quickly. A 21-in. pipe is sufficient for the gas of two pans and two blind roasters. The single pipes are made as long as practicable, so as to have fewer joints. It need hardly be said that the pipes must be supported in such a way as to enable the joints to be made good all round, and that the sockets of the pipes should be at the highest point, if there is any fall.

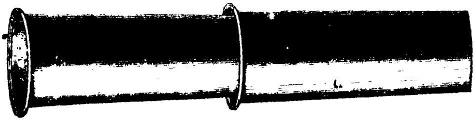


FIG. 67.

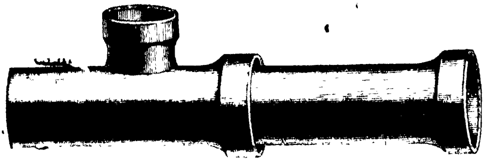


FIG. 68.

The usual material of the pipes conveying hydrochloric-acid vapour is stoneware or fireclay. It is not easy to get pipes resisting both the changes of temperature and the acid gases. This, however, is the maker's fault; for good pipes can be made without any special difficulty, if sufficient care be taken, as is proved at the Tyne Chemical Works at Gateshead-on-Tyne (formerly Messrs Allhusen & Sons), where their own pipes are made, and to whom neighbouring factories readily paid *twice* the price asked by ordinary pipe-makers. Their pipes were made of fireclay by hand, without glazing, and before using were boiled in tar for at least two days. Most other pipes are machine-pressed. They are always best left unglazed and boiled in tar, because they then resist better both acids and cracking than glazed pipes, which cannot be boiled in tar; but even the tar-boiled pipes frequently crack. In Lancashire pipes made of ordinary stoneware, "sanitary pipes," are sometimes employed. Excellent pipes are those made by Messrs Doulton, of Lambeth, of very carefully prepared stoneware. They are much thinner and longer than ordinary pipes and cool the gas very well; they also last a long time.

For some time *glass pipes* were in much favour in many Lancashire works; their introduction is due to Mr Alfred Fletcher. Owing to their thin walls, they cool the gas very well indeed, and do not easily crack, especially if protected from rain and snow by a shelter. They are always made a little tapering; and the thinner end of one is put into the thicker end of another. They can only leak at the joints, if badly cemented, like *all* pipes; but they are perfectly air-tight in their body; whilst earthenware pipes frequently allow the gas to escape all over, or even liquid to ooze out. The latter occurs with Lancashire stoneware pipes much more than with porous fireclay pipes boiled in tar. Glass pipes are as cheap as stoneware pipes. Their cooling action, in a string of 300 ft. length, was found to reduce the temperature from 155° C. at one end to 57° C. at the other end, with an outer temperature of 7°. If a fine jet of water is allowed to enter at the hotter end, up to two-thirds of the acid condenses in these pipes themselves. They are employed not only for pan-gas, but also for blind roasters, and, if properly supported, stand better than any earthenware pipes. Recently glass pipes have come more into favour, and many works have adopted modern forms of water-cooled glass condensers.

The official *Alkali Works Report for* 1887, p. 50, states that in the fourth district remarkably good results were obtained, partly through the increasing introduction of plus-pressure furnaces (see above, p. 119), partly by replacing the underground gas-flues by overhead sets of glass pipes. Lunge received a specially good account of the glass pipes made by Pilkingtons at Widnes, which are annealed with particular care. The glass tubes made by Moncrieff of Perth are very good for use as cooling pipes.

In the Report for 1884, p. 86, a factory is mentioned which possesses for its ten saltcake-furnaces (nine of which are Deacon's plus-pressure furnaces) not less than 2170 ft. of upright glass cooling-pipes. The following temperatures of the gases have been observed there:—

On entering the glass pipes	133°
„ „ coke-towers	62°
„ leaving the „	47°

In the Report for 1885 (p. 57) we find the following statement concerning a set of pipes 320 ft. long and 12 in. wide:—

Temperature on entering the pipes	105°
„ „ the coke-towers	64°
„ „ leaving the „	51°

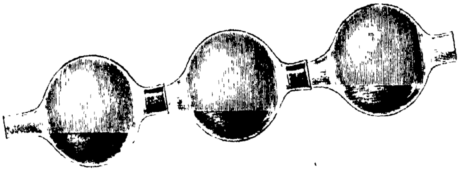


FIG. 69.

The fact that glass really has an excellent cooling action can be observed at several American works whose condensing-apparatus (certainly only for cylinder apparatus) consists exclusively of glass receivers, holding about 12 gallons each, inserted into one another, as shown in Fig. 69, which act in reality as surface-condensers. The water contained in them is renewed from time to time by a stream from above. Such a slightly inclined set of about twenty receivers is connected with a larger stone receiver from which a second row of glass receivers rises up in the same angle. This apparatus, although decidedly crude and only adapted for very slow work, is said to furnish strong acid, and to allow nothing to escape; but this is very doubtful.

It is a very common practice to employ some of the pipes cut through lengthways, so that the upper half can be taken off; of course, for use, the two halves are cemented together.

If one such pipe is put in about every three yards, the cleaning of the series from the accumulating deposit is much facilitated.

The whole series of pipes, both for pan and roasters, is always arranged in such a manner that it is first taken straight up to a sufficient height for getting afterwards a continuous fall, towards the first tank or receiver, or in the absence of these towards the condenser itself. This is done to prevent the running back of any condensed acid.

Even with blind roasters, as we have seen, it is preferable to employ separate pipes for pan and roaster; for open roasters this is absolutely necessary. With these the employment of earthenware pipes immediately behind the furnace is not advisable, owing to the great heat; either brick flues or cast-iron pipes are preferred.

Brick flues are sometimes carried underground, but those underground flues do not fulfil one of the principal functions of condensation, viz., good cooling. Better service is afforded, but only for the vertically ascending part of the gas-flue, by flues made of specially moulded firebricks, as shown in Fig. 70. They are shaped to the sweep of the flue, and provided with feather and groove; if very fine tar-and-pipeclay cement be put into the joints, the flue will be very tight and stand well without repairs.

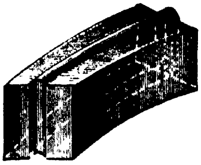


FIG. 70.

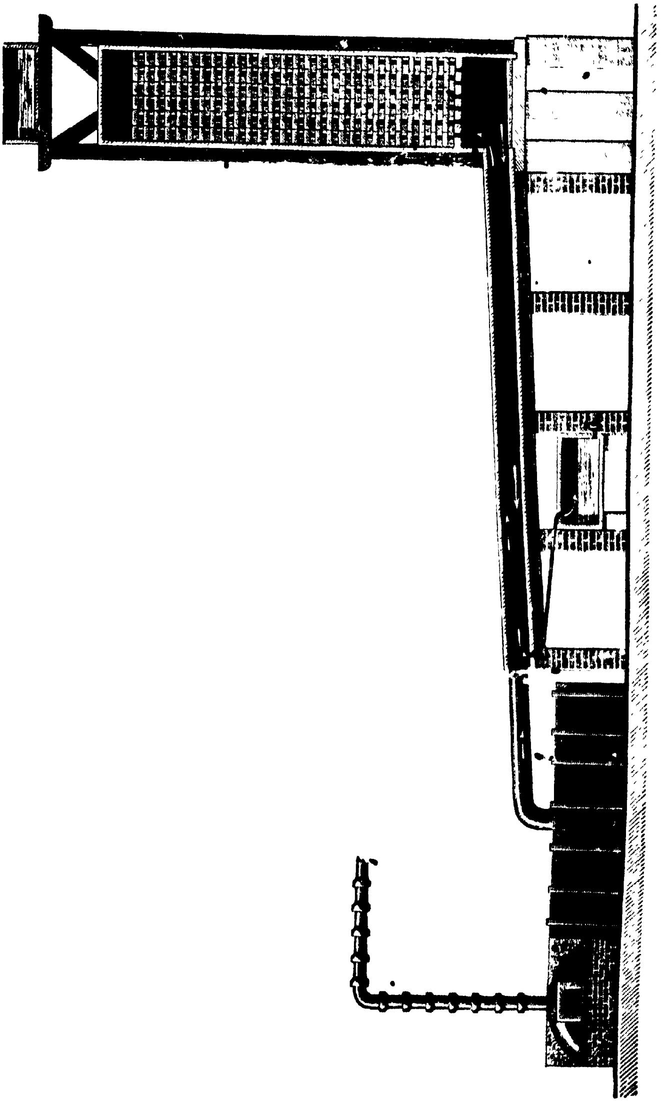
At the larger English works *cast-iron pipes* are very frequently employed for conveying the furnace-gas from open roasters. Of their cooling action we have treated on p. 253. They may be employed without any danger of being destroyed by acid so long as the gases are hot; and just their excellent cooling action is their greatest recommendation. But as soon as the current of gas has cooled down so far that liquid acid might be condensed, say to 100° or 120° C., the metal pipes must be discontinued, and the further conveyance of the gas must take place through earthenware pipes. With the assistance of metal pipes, stone cisterns may be employed even for open-roaster gas, which otherwise would crack them too easily. The actual length for which metal pipes may be employed without danger of too much cooling and subsequent corrosion depends entirely upon the style of work in the furnace. The more salt decomposed in a certain time, the longer will the current of gas remain hot enough for metal pipes. Usually 60 to 100 ft. of metal piping form the limit which must not be exceeded; but occasionally the length may reach 300 ft.

The metal pipes are usually cast in lengths of 9 ft., and 2 ft. to 2½ ft. wide; they need not be above 1 in. thick. They are either cast with a socket at one end, into which the other end fits, or with straight ends, over which a loose ferrule is slid and cemented on both sides with tar and china-clay. If the pipes have to be cleaned out, the cement is softened by heating, the ferrules are slid sideways, and the pipe is lifted by means of a winch, so that both itself and its neighbours become accessible inside.

There is always some deposit formed in the iron pipes; but the amount varies much: it is sometimes so great that they have to be cleaned out once a week, sometimes so little that cleaning them out once a year is sufficient. The following analyses (from the *Alkali Act Reports*) show that this deposit consists of sulphate carried along by the gas, together with the products of the action of sulphuric acid upon the iron, this acid being precipitated in a liquid form long before the HCl:—

Ferric oxide . . .	19·866	26·946	6·400	19·483	27·407
Alumina	3·171	4·614	3·545	3·905	4·689
Lime	0·371	0·486	2·110	1·383	0·482
Magnesia . . .	0·414	0·298	0·751	0·708	0·281
Soda	11·311	2·808	24·093	12·653	6·003
Silica	6·049	3·309	13·020	3·292	4·166
Sulphuric acid (SO_3) .	53·212	48·077	48·695	34·286	26·220
Chlorine	2·141	2·034	0·092	2·278	20·409

Flues made of stone flags are also employed for roaster-gas; the stone should not only be able to resist the acids, but also the changes of temperature. It is a very good arrangement to give the flue a little rise towards the coke-tower, and to allow the acid of the latter to flow down the bottom of the flue; this unites all the advantages of acid-tanks with thorough cooling. At the other end of the flue the acid is got as strong as pan-acid, but, of course, less pure. The sketch, Fig. 71, will make this clearer. The upper arrows show the path of the gas, the lower arrows that of the liquid.



Circular flues, made of two semicylindrically hollowed blocks of stone (Fig. 72), are used at some German works with great success; also troughs excavated in blocks of stone, with stone lids (Fig. 73).

If (from local causes) the condensers are considerably less than 100 ft. away from the furnaces, the necessary length of pipes for cooling is obtained in this way: they are first carried a little downwards so as to prevent condensed acid from running back into the pan, then they are carried upwards for, say, 50 ft., and down again, and ultimately into the condenser. In the lower elbow there must be a hydraulic lute for the condensed

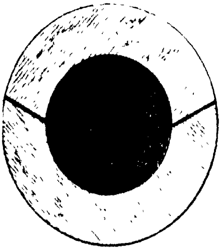


FIG. 72.

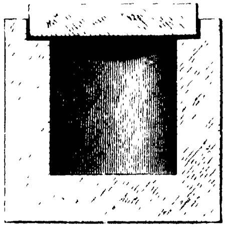


FIG. 73.

acid, which is very impure. This arrangement is met with both for pan- and roaster-gas, with earthenware, iron, stone, or brick flues. It is also employed for Newall and Bowman's water-spray process (cf. *infra*). On the largest scale this multiplication of cooling-surface is employed for the very hot gas from Hargreaves's saltcake process, where the pipes are not only carried a great length, but are also multiplied by admitting the gas into a long trough, from which a number of parallel strings of pipes convey it into another similar trough communicating with the condensers. Even for ordinary saltcake-gas such an arrangement is met with here and there.

Sometimes, but rarely, the gas-pipes have been placed in cold-water troughs; in such a trough of 24 ft. length the gas was cooled from 250° to 180° C. This takes much water, and cannot compete with air-cooling in cheapness. This plan is further developed in Fryer's condenser, to be described further on.

A very peculiar kind of preliminary cooling of hydrochloric-acid gases is practised by the Salzbergwerk Neu-Stassfurt (Ger. P. 55461). Here the gases are cooled from 200°-300° down to 100°-150° by passing them through a tower or flue in which they are brought into contact with heat-absorbing solid salts, not decomposable by hydrochloric acid. This is best done by salts containing water of crystallisation which melt with absorption of much heat, such as the chlorides of calcium, magnesium, or strontium. The liquefied salt flows off through a hydraulic lute, protected against cooling, so that the salt does not solidify there but only outside, whereupon it can be used over again. The cooling-apparatus must be kept hot enough not to condense any liquid hydrochloric acid, which would run away with the above-mentioned chlorides. The cooling apparatus employed at the Aussig works will be described later.

Stone Cisterns or Tanks.

At first the condensation of the hydrochloric acid gas was attempted entirely by means of *cisterns* filled with water, over whose surface the gas was conducted. In order *completely* to condense any quantity of hydrochloric acid in this way, the water-surface should be very large indeed; and this is all the more troublesome as metal or wood vessels cannot be employed, and even brickwork set in pitch stands very badly: so that ultimately only the very expensive stone cisterns remain available. This condensing-arrangement would be practically impossible for any large factory, not only on account of the cost, but also of the large ground-space required. Cistern condensers therefore went out of favour; and, in England especially, are less employed than they deserve to be, if used in the proper way, viz., only as supplementary to coke-towers.

Different systems may be employed for constructing stone cisterns. In France and Germany they are sometimes hewn out of one large block. This for large sizes is enormously dear, and if the cisterns crack, it is often impossible to repair them. We shall therefore describe only the two constructions usual in England, and represented in Figs. 74 to 77.

In the first construction the edges of the sides are bevel-jointed; they are bound together by cast-iron brackets and tightened by india-rubber cord. Fig. 74 shows such a tank as viewed from above, after taking away the cover; Fig. 75 is a side elevation, Fig. 76 the bottom-stone, and Fig. 77 one of the four side-stones as they have to be dressed by the mason; Fig. 78, *a* is a side elevation, and *b* a horizontal section of a corner bracket. In the bottom-stone a shallow groove, 1 in. broad × ¼ in. deep, is made in the middle of the place intended

FIG. 74.

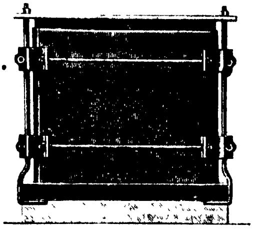


FIG. 75.

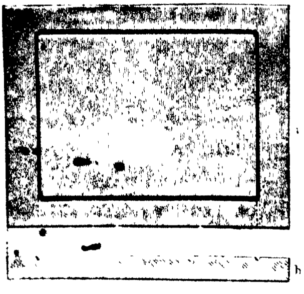


FIG. 76.

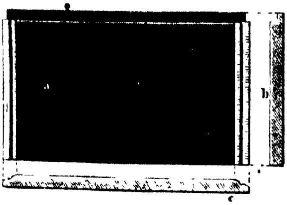


FIG. 77.

for the side-stones, for receiving the india-rubber cord. As the stones are rarely sufficiently even, a band of 6 in. width is first dressed smoothly all round the stone, and the groove cut into this afterwards. The side-stones are dressed quite smoothly below, and a similar groove is cut in. Their two lateral edges are dressed as shown in the diagram; but only the bevelled part, which has to receive the groove for the joint, must be dressed smooth. The upper edge receives a recess for the cover. This itself does not require any dressing; it may also consist of two halves, while the bottom-stone must not. The cover is provided with a man-hole. When the bottom has been dressed and placed exactly level on its bed, an endless ring of 1-in. solid india-rubber cord is put into the groove, to whose square shape it is, of course, easily fitted, and is fixed at the four corners by tacking down. In these corners afterwards, by cutting in, ⅝-in. india-rubber cords are fixed, equal in length to the height of the sides; they afterwards serve for tightening the side-joints, and in the meanwhile are held by strings from the top. The four side-stones are singly put into their places, and fixed by wedges a little above their final position, so that they all incline outwards against wooden props. They are then carefully put into their proper places, exactly plumbed, and the horizontal and vertical india-rubber cords drawn into their grooves, whereupon the wedges are drawn out and the weight of the stone is allowed to press upon the india-rubber. The sides still remain supported, till they have been bound by the brackets, and held together by 1-in. round screw-bars. The binding is troublesome work, since every single piece has to be supported till the last bolt is in its place. Where the brackets touch the stones, small recesses are cut in and strips of lead put between the stone and the cast-iron bracket, which equalise the pressure.

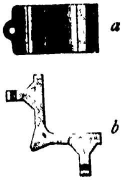


FIG. 78.

Now the cover is put in, and the joint made good in its recess by tar and china-clay; if it consists of two halves, the joint is made in the same way. The pressure of the sides on the india-rubber cord is not sufficient to make the tanks acid-tight; therefore two cross-bars (about 4 in. × 1½ in.) are put on the cover, through whose ends pass screw-bolts, which bend off at a right angle below the bottom-stone, and on screwing the nuts down hold the cover, sides, and bottom tightly together. In Fig. 77 the places are visible where these four perpendicular bolts are fixed, and in Fig. 79 one pair of these along with the cross-bar.

In the second construction two opposite sides fit into grooves of the end-stones at right angles with them; all four rest in grooves of the bottom-stone. The binding only takes place from one end to another by means of long bolts connecting the projecting parts of the end-stones; and the joints are always made good by tar and china-clay cement caulked in. Fig. 79 shows a cistern of this kind in perspective, but preserving the proper dimensions. Only, in order to show clearly the way in which the sides and ends are feathered and grooved together, the upper recess, which must be made for the cover-stone, has been omitted. Fig. 80, *a*, shows the bottom-stone from the top; Fig. 80, *b*, in section, Fig. 81, *a*, one of the sides, seen from within; Fig. 81, *b*, the same in side elevation; Fig. 81, *c*, top elevation; Fig 81, *d*, bottom elevation. The recess for the cover is shown in Fig. 81, *b*. Fig. 82, *a*, is an elevation of one of the ends, and Fig. 82, *b*, shows the end piece from below. In Fig. 81 are seen the grooves for the sides and ends, $4\frac{5}{8}$ in. broad and 1 in. deep. In the middle of each is a V-shaped groove (1 in. side), which, together with a corresponding bottom-groove of the sides and ends, forms a channel for the cement. The two outer parts of the ends, where no joint is necessary, are left rough at the bottom, and are perforated with two bolt-holes each Besides, the ends have each a perpendicular groove, $4\frac{5}{8}$ in. wide and 1 in. deep, with a V-shaped recess in the centre, just like that in the bottom; the edges of the sides enter into this groove. The sides themselves only have a V-shaped recess all round the two sides and the

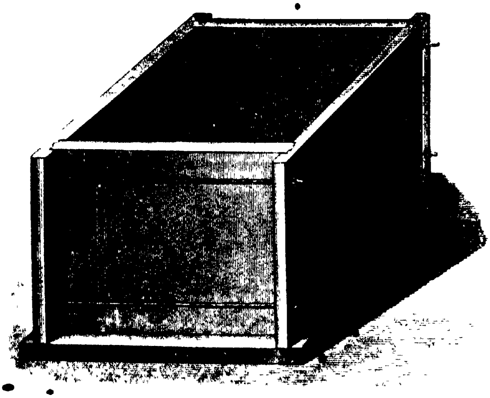


FIG. 79.

bottom, since they enter into the grooves of the ends and the bottom. Both sides and ends have a recess for the top-stone on their upper edge. The thickness of the sides and ends in this case is about 4 in., so that the grooves are wide enough for caulking with some cement.

If a cistern of this kind has to be put up, the bottom is levelled, the sides and ends are placed a little above their final positions and provisionally supported. Then the bottom grooves are completely filled with tar and china-clay cement, and the sides and ends let down into them; of course a great deal of cement is squeezed out, and is stemmed inside and outside into the space left between the stones and the margins of the grooves. First, however, two days are allowed to elapse for the cement to harden a little. For the upright joints the process is somewhat different. The cement is made into small

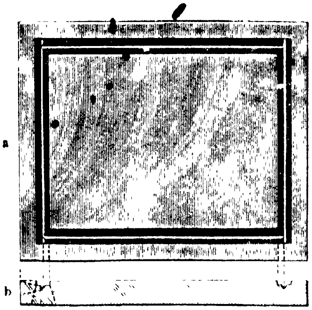


FIG. 80.

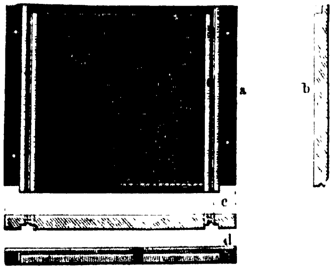


FIG. 81.

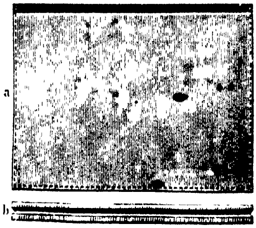


FIG. 82.

balls, which are dropped into the lozenge-shaped groove, and rammed down with a hot iron, a good deal of cement getting squeezed out sideways; this is continued till the top is reached. Here also the cement squeezed out is stemmed into the small joints remaining in the grooves. The four screw-bolts connecting the two ends are put in and are tightened up as much as possible. In order to divide their pressure all over the stone, they press upon an iron bar 4 × $\frac{3}{8}$ in., or upon a piece of pitch-pine 4 × 6 in. The cover may be simply bedded in cement in its recess; the cross-bars and vertical screw-bolts are not required here, as the bottom-joint is tight without them. This, however, only holds good of the acid-cisterns, with which we are occupied at present; in the case of the chlorine-stills, otherwise built in exactly the same manner, it is safer to screw the top down, on account of the steam-pressure.

The question now arises, which of the two systems just described is preferable. In the first system a somewhat smaller stone surface is required for the same cubic contents, and the dressing of the stones takes less time, because the large grooves have not to be made; the bevelled edges, certainly take a good deal of work. On the other hand, much more iron is required than in the second system, viz., eight screw-bolts, instead of four for the sides, eight corner brackets, and the cross-bars and screw-bolts for the tops. Once complete, these systems last very long without any repair; but if they have to be taken to pieces, the india-rubber cord cannot be used again. With the second system more stone and labour for cutting are required, but a little less labour for putting them up; the saving in ironwork is very considerable; and the tar and china-clay cement is also much cheaper than the india-rubber. The joints are not quite so much to be depended upon as in the first system; and stemming the joints is now and then necessary. Everything here depends upon the care and skill of the first builder; Lunge saw cisterns of this kind which after five years' use did not show any signs of leaking.

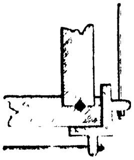


FIG 83

The cisterns constructed on the second system are, as a rule, somewhat cheaper than those made on the first. The first system is principally used in Lancashire, the second on the

Tyne. It would appear that there is not much to choose between them, but the second (groove-joint) system is probably preferable.

A combination of both constructions consists in employing grooved joints and tar and china-clay, but joined by corner brackets and the same number of screw-bolts as in the bevel joint system. The sketch (Fig. 83) will make this clear. Thi style was selected in a special case from fear that the direct pu of the bolts upon the projecting ends might be too strong but later on the stills were built just in the manner illustrate in Figs. 79 to 82, with grooved joints.

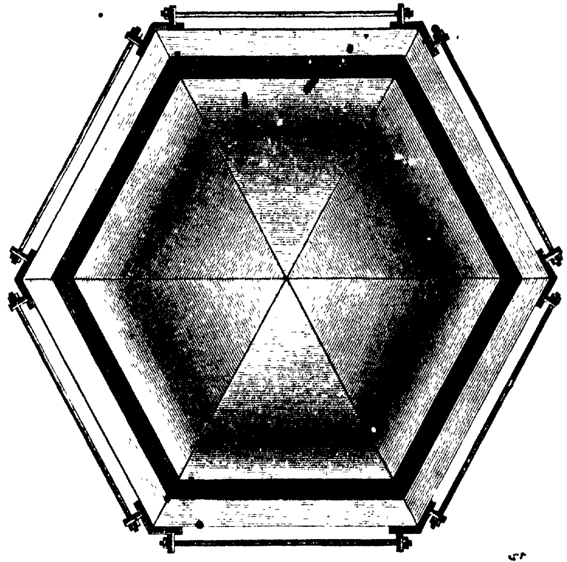


FIG. 84.

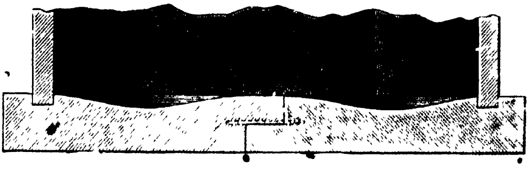


FIG 85.

The bottoms of the largest hexagonal or octagonal stone towers cannot be made of a single stone. They are composed of segments, whose joints are made tight by india-rubber cord, as described on p. 263; on the outside the whole is braced together by a framework of cast-iron cramps and screw-bolts, as shown in Fig. 84. The grooves for the side-stones are shown in Fig. 85. The joints are stemmed with a high-melting tar-fireclay cement (p. 265). If bottom-stones are thus composed of two halves (which is the case even with acid cisterns), these are made with overlapping rabbets, as shown in Fig. 85, and are joined by the hardest tar-fireclay cement, or even better by pouring in a mixture of melted brimstone and sand. Cramps on the outside prevent the stones from parting. In the case of coke-towers each of the halves is dished for running off the acid.

The *thickness of the stones* depends upon various circumstances, and in the first instance on the quality of the stone. In the North of England "Yorkshire flags," from Halifax and Southowram, are very much used, consisting of a sandstone that resists hot acids even without boiling in tar, which, on account of its dense grain, would not do it much good. It splits very evenly, so that flags of large size and of any thickness can be obtained by the simple use of the wedge. Of this stone much thinner slabs can be used than of more porous and less firm sandstones, of which thin plates are frequently as dear as or dearer than thick ones. A thickness of 6 in. for the bottom (12 in. for condensers), 4 in for the sides and ends, and 4 or even 3 in. for the tops will do; frequently thicker stones are employed, but without any good reason. Although this stone is not boiled in coal-tar, it is advisable and costs very little to paint the tanks well with tar or, still better, with varnish made from tar.

In the Tyne district also a very good siliceous sandstone is found, which is employed for acid-cisterns, condensers, and chlorine-stills. Its denser varieties, such as the Heworth stone, do not require boiling in tar. This stone does not split in plates, and must be cut out of the rough; it is rarely employed below 6 in., usually 7 in., for the sides, and 10 to 12 in. for the bottom. It is not so readily cracked by changes of temperature, and does not scale off under the influence of hot acid, as Yorkshire stone does in the course of time. A similar stone is found in Germany, near Herdecke and Wetter in Westphalia, and at several other places.

In France volvic lava, from Clermont-Ferrand, which has already been mentioned in Vol. I., p. 645, is generally employed. It must be borne in mind that this material, from which large slabs, blocks, and whole cisterns can be made, frequently resists both very considerable changes of temperature and the strongest hot hydrochloric acid, but sometimes samples occur which allow the acid to "weep," or which even crack. Care must therefore be taken in buying them.

G. E. Davis[1] quotes analyses of two kinds of Yorkshire flags, which seem to prove that this is not altogether a siliceous sandstone.

	Yorkshire Flags		Blue Bricks.	Common Bricks.
	I	II		
Silica	86·52	80·50	60·70	62·40
Alumina	7·36	11·25	24·00	26·46
Ferric oxide	1·54	3·60	14·60	2·34
Lime	1·08	0·61	0·14	0·14
Magnesia	trace	0·12	trace	..
Manganese protoxide	trace	trace	...	.
Sulphur trioxide	0·45	0·77	...	..
Carbon dioxide	0·60	0	..	..
Water	1·88	2·64	..	..
Ferrous sulphide	0	trace	...	
Alkalies	...	...	1·00	1·00

Any open varieties of stone must *be boiled in coal-tar*, always *after* being dressed by the stone-mason; for sandstone after boiling in tar is too hard to be cut. For this purpose an iron pan is used, over which a travelling crane runs for putting in and lifting out the stones. The tar must be deprived of its most volatile constituents by boiling, but it should not be boiled down to a very thick consistence, because the pitch thus formed will not penetrate sufficiently into the stone. The stones (or the whole tanks if made in one piece) must be left lying at least a week in the boiling hot tar. Even then the tar barely penetrates half an inch into the stone, but still imparts to it great resistance against acids, as well as against changes of temperature, rendering it as it were tougher.

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[1] *Chem. Trade J.*, ii., p. 375.

Better than ordinary boiled-down coal-tar is a varnish made by depriving tar of its most volatile oils and of anthracene, and bringing it to the desired degree of fluidity by mixing more or less heavy oil with it. This article is largely sold in Germany as "prepared tar."

Acid-proof slabs, artificially prepared, with metallic background have been patented by C. Kellner (Ger. Ps. 56974 and 68168). He first coated iron with a mixture of cement, aluminium silicate, and water-glass; later on he prescribed putting upon the above-mentioned coating a sheet of lead, which is joined with those of the other slabs at the edges by rabbeting or burning; upon this he again places the above mixture and presses sheets of glass into this. It is not likely that this composition will be introduced in the manufacture of hydrochloric acid.

Engels and Nickel (Ger. P. 67802) manufacture cisterns from acid-proof mixtures by embedding in the latter corrugated sheets of metal, which impart to the vessels the required strength, without coming into contact with the acid.

E. de Haen (Ger. P. 197074) manufactures acid-proof vessels by pressing tantalum hydride into moulds and heating the moulded pieces in a vacuum to a white heat, whereby metallic tantalum is formed.

"Obsidianite" is the name given to an artificial acid-proof non-porous material, recently come into use in the place of volvic lava, etc. According to *Chem. Trade J.*, 1909, vol. xliv., p. 101, it is "vitreous silica," costing half as much as volvic stone, but lasting much longer, and having a much greater breaking strain, viz., 3½ tons per sq. in. Sir F. Nathan has built a Kessler plant entirely of this material at Waltham Abbey, in which also the acid lutes are worked in the stone itself so that no porcelain lutes are needed.

Woulfe's Bottles (stoneware receivers).

The condensation of hydrochloric acid in Woulfe's bottles or receivers (bombonnes, touries) is not always employed in England; but in France, Germany, Austria, and Belgium it is the most usual plan, partly with, partly without a small coke-tower at the end. Most good factories have the latter as well.

These receivers are large stoneware bottles, provided with two large necks and one small one on the top, and with a short branch for a tap at the bottom, mostly also with side branches for mutual communication. It is very important that both in the manufacture of the receivers and in the previous separation

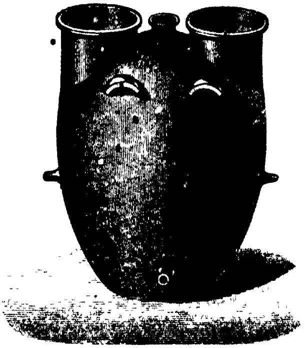

FIG. 86.

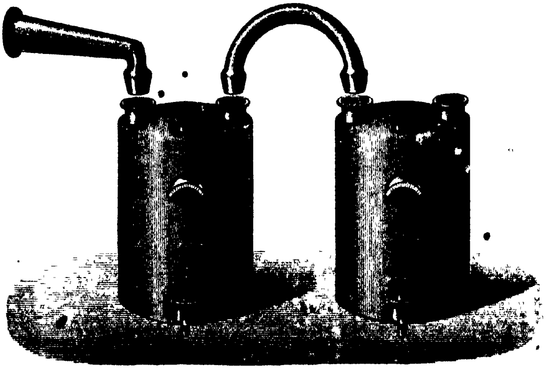

FIG. 87.

of the clay the greatest care should be exercised. Of course the clay should be entirely free from lime; it must, moreover, be well levigated lest any small pieces remain in it, which either in burning, or, if not then, certainly afterwards in use give rise to cracks. Even then not all varieties of clay are adapted for this use, but only good fireproof kinds. In moulding and burning also the greatest care must be taken. On burning, the heat, as with all real stoneware, must be increased up to the point at which the mass frits and is semivitrified; even without an enamel it should not allow any liquid to pass through; and of course it should have no cracks. Receivers which really fulfil all fair requirements and do not crack by changes of temperature can only be got from a few places.

Good stoneware receivers, etc, are supplied in England by

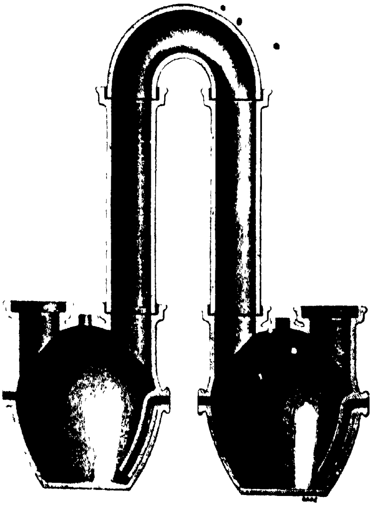

FIG. 88.

Messrs Doulton of Lambeth, the Leeds Fireclay Co of Leeds, and by several other makers. In France, they are obtainable from the Beauvais potteries. The shape usual in Germany is shown in Fig. 86, the English one in Fig. 87. Fig. 88 shows a later English form made by Messrs Doulton. Decidedly the best shape from a constructional point of view is that made at Aussig (Fig. 89, p. 276). The bottles are about 3 ft. 3 in. high; the bellied continental shape is in the centre from 2 ft. 2 in. to 2 ft. 8 in. wide, the cylindrical English shape about 2 ft. wide. They hold from 36 to 38 galls.

A new kind of moulding has been introduced at the Aussig Chemical works. The receivers, etc., are moulded in plaster-of-Paris shapes from clay slabs cut off by a wire from a block, instead of on the potter's wheel. They are made so accurately and neatly that the best eye cannot discover the original joints, which on burning would become wider, of course.

The two upper wide necks serve for receiving the siphon-shaped connecting-pipes, in which the gas is carried in and out; they are from 6 to 8 in. wide. The middle neck, usually stoppered, serves for pouring in water; it is 2 in. wide, as is also the lower one, into which a stoneware cock of ½ to ¾ in. bore is ground. The latter is not required if side branches are present through which each bottle is connected with its neighbours; only the last of them in that case needs a cock. There is no difficulty in grinding in the cocks so that they close perfectly tight; but in consequence of bad work they frequently leak at the joint. It is not easy to mend matters by cement, as there is no chance of stemming any in, as can be done in tanks made of stone flags. The acid can also be drawn off without any cock by a siphon put into the upper neck. Such siphons are made of gutta-percha and last a long time, as faulty places can be easily mended by cutting a piece out and putting another one in. Gutta-percha can be soldered perfectly by means of a hot iron.

The receivers are always combined in series such as have been figured on p. 77, in describing the older saltcake-furnaces. Usually there are two rows for each pan, and as many for each muffle. Two rows are employed, because the connecting-pipes cannot easily be made wide enough to afford sufficient draught with a single one. They are made of the same material as the bottles themselves, and a little narrower than the necks, but provided with a flange or a conically widened-out end (Fig. 86), lest they should go down too low. Often they are made pretty high, say 3 ft., in order to cool the gas. The pipes are cemented into the bottle-necks with the same *cement* that plays such an important part in the condensation of hydrochloric acid, and which has been frequently mentioned above. It is made by well kneading-up thickened coal-tar with as much finely ground china-clay or pipeclay as it will take up, and well beating the mixture with wooden mallets till it has become a perfectly homogeneous plastic mass, which is moulded into brick-like blocks, and can be kept for some time. It is called at the works "black stuff," sometimes (in Lancashire) "barytes." In larger quantities (for instance, if a whole condensing-plant has to be built) this cement is made in the cheapest and best way by grinding up the ingredients under edge-rollers, for instance in a chalk-mill. Before use it is moderately warmed up and stemmed into the joints by means of bits of iron. It gives very tight, acid-proof joints, and in time becomes harder when heated, of course not up to a red heat. Where it cannot be stemmed in, it must be used in a softer state, but then it does not make such strong joints.

A less resisting, but more elastic cement is obtained by melting up coal-tar with some rosin, and kneading it with finely ground pipeclay and sand. Of course asbestos-silicate cement can also be employed

Sometimes the receivers are connected by hydraulic lutes, as will be shown later on (Fig. 89). In this case the pipes are not so firmly fixed, but they can be very quickly put in and taken out if need be

The first receivers of each row are always connected by a forked stoneware pipe with the gas-pipe of the pan or muffle, unless the gas first passes through a small tower in which most of the sulphuric acid is condensed by injected water, and the gas is so much cooled that the first receivers are much less subject to cracking. The last pipes go into a chimney, or (much better) into a coke-tower (see below).

If each bottle is filled and emptied separately, the whole series stands on the same level. The acid-gases are nearly deprived of their hydrochloric acid and other constituents soluble in water in the first few bottles, and in these a strong acid is formed, showing in winter 34° to 36° Tw., in summer 28° to 30° Tw.—the latter partly because acid of equal percentage of HCl at a higher temperature occupies a larger volume, partly because in warm weather it is not possible to make such a strong acid, owing to the decreasing solubility of HCl in water with increasing temperature. The later bottles of the series then serve for absorbing the small quantities of HCl which have escaped condensation in the first bottles, and only very weak acid is formed in them. Whilst, therefore, the first bottles can be daily emptied and refilled with water, and yet furnish strong acid, the later bottles not only have to stand much longer, but they cannot wait till their acid has got up to strength, since in that case much HCl would escape condensation. Their contents must therefore be regularly withdrawn in the state of weak acid and filled into the first bottles, in order to get up to strength in these, whilst fresh water is put into the last bottles.

This process requires much labour, and on emptying and refilling the bottles the draught in the decomposing-pans and furnaces is very much interfered with; thus much acid vapour escapes from these and from the open necks of the bottles. All the best factories therefore now work differently. Usually the bottles are placed terrace-fashion on an inclined plane. Only the top bottle is fed with water, and acid is only withdrawn from the bottom bottle. The current of acid-gas travels in an opposite direction, first into the strongest bottle, whose contents it entirely saturates, then over acid less and less concentrated, and ultimately over pure water. This is evidently a rational arrangement. Without any manual labour water is continuously run in at one end and strong acid is run out at the other. But if the acid has at once to be filled into carboys, the labour required for this has to be furnished. Some arrangement must in this case exist for the liquid to flow out of each bottle into the next lower one. But it is much better if the bottles are combined in such a way that the acid lying on the *bottom* of the higher bottle, being a little heavier and more concentrated than that at the top, runs into the next lower bottle. The way in which this is done will be shown very clearly later on, in describing the Aussig apparatus. One of the two side openings (Fig. 89) is connected with a moulded-in stoneware pipe, which goes almost down to the bottom of the bottle, and causes the outflow always to begin from there. The connection between two bottles is made by short glass tubes, which are joined to the thickened edges of the side branches by strong elastic tubing: or the side branches are moulded so as to bend upwards, and are joined by small glass siphons reaching from one bottle to the other. The simplest plan is to put into the side openings india-rubber corks, through which passes a short glass connecting-tube.

It is sufficient to place each bottle 1 in. below the preceding one, so that a whole series requires only about 3 ft. fall.

Sometimes, in order to cool the gases better, the receivers are placed in a tarred wooden trough into which cold water runs at one end. This, however, is not easily combined with the terrace arrangement just described. In this case it is still possible to run water upon them from the outside, but at a considerable risk of cracking them. At all events the bottles ought to be protected against the direct action of the sun by a light roof.

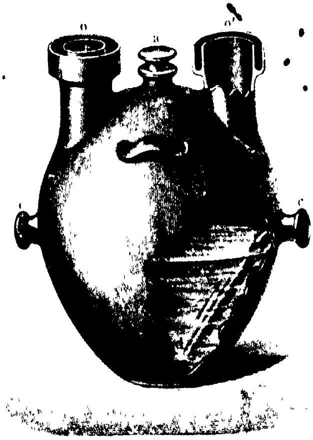

FIG. 89.

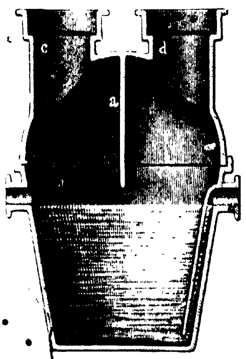

FIG. 90.

Other Shapes of Stoneware Receivers.

Wimpf (Ger. P. 58413) makes hydrochloric acid receivers in two parts, as shown in Fig. 90. The lower part contains the acid; the upper part is provided with a partition, *a*, between the two necks *c* and *d*, which compels the gas to come down close to the acid.

Touries with an internal cooling-pipe are made by the Deutsche Ton und Steinzeugwerke, Charlottenburg (Ger. P.

means of air, pass through the bottle in a slanting direction, so that draught is produced without artificial means; or else they may be attached to mechanical aspirating or draught apparatus.

Walter & Lehmann (Ger. P. 88444) enlarge the surface of the liquid in the receivers by placing porous earthenware cylinders inside them.

The receivers constructed by R. Cellarius (Ger. P. 106023, of 1899) possess great advantages over the ordinary touries, and have been introduced in some of the best-managed factories. We describe them here in the first instance from communications made by the inventor.[1] He first discusses the drawbacks attached to the ordinary touries. These labour under several disadvantages which prevent a complete absorption of the HCl gases by the water. The proportion of the surface to the volume of the water is very unfavourable, so that the heat liberated by the absorbing process is dispersed too slowly. For the same reason outside cooling by water is not very efficient, apart from the fact that the ordinary shape of these bottles makes it very inconvenient to arrange them in cooling-boxes. As the liquid acid formed proceeds through the set of bottles, the stronger acid ought to be forced forward by the weak acid; but this process is not perfect, the weaker and stronger acids getting constantly mixed. Experiments have proved that ten volumes of water are required to force one volume of acid of 32° Tw. out of a bottle.

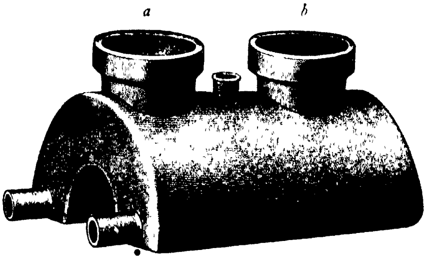

FIG. 91.

All these drawbacks are avoided by the Cellarius receivers, which are made in two different forms. The first of these consists of two horizontal semi-cylinders, connected with each other concentrically. The longitudinal connection forms the bottom of the receivers. These are made in two shapes. The first of these is shown in Fig. 91; it is employed in those cases where there is no arrangement for cooling by water, and where no acid above 36° Tw. is required. The liquid enters on one side just above the bottom by neck *a*, passes over the inner arch and leaves by neck *b*, just above the bottom on the other side.

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[1] *Z. angew. Chem.*, pp. 104 *et seq.*

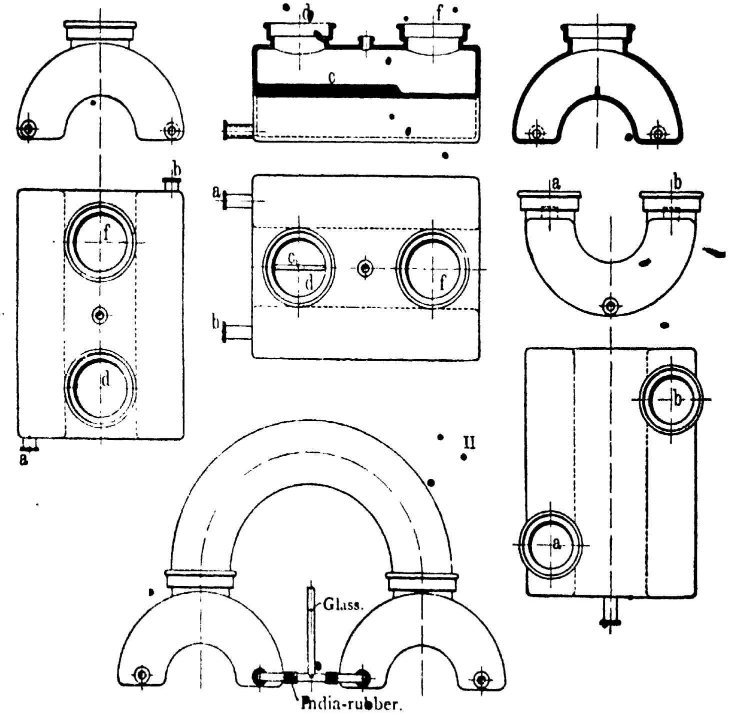

FIG. 92.

The second shape is shown in Fig. 92; it is used where cooling by water is employed, and acid up to 40° Tw. is to be made; but it may be, of course, used also without water-cooling.

Here the necks *a* and *b* are placed on the same side of the receiver. On the inner arch a projection, *c*, is formed which reaches three-fourths of its length. The ordinary gas-necks, *d* and *f*, are placed on the outer arch.[1]

The Cellarius receivers have the following advantages over the ordinary Woulfe's bottles:

1. The proportion between the surface and the volume of the liquid is several times more favourable.

2. The second shape (Fig. 92) is easily mounted in water-cooling boxes. The necks for the acid are made tight by india-rubber washers, and the receiver is placed in water up to the gas necks. Thus not merely is the acid cooled in a thin layer, but the gas is also compelled to travel along water-cooled surfaces.

3. By placing the necks for the liquid at the bottom, on both sides of the inner arch, the stronger acid is forced over to the next receiver, without getting mixed with the thin acid. Thus acid of 32° Tw. is completely forced over by only 1½ times its volume of water.

4. Each particle of liquid must travel twice the length of the receiver, and up and down the same, before it can get out. The weaker acid rises above the inner arch and lies on the top of the stronger acid, without mixing.

5. The necks for the liquid and the connecting-tubes being always immersed in water, no air-bubbles are formed, which very frequently cause unbearable trouble with the ordinary receivers.

6. On the surface of the liquid within any kind of receivers there is always a floating skin formed, more or less according to the quality of the salt, of the sulphuric acid employed (waste acids), of the grease and the cement. This skin consists essentially of resinous substances, mixed with finely divided carbon, and of tar. Generally it does not materially interfere with the absorption, but it becomes troublesome after some time and when using inferior raw materials. The skin must then be removed, which in the case of ordinary bottles involves stopping the process. But with Cellarius receivers it can be done at any

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[1] Th. Meyer claims in *Z. angew. Chem.*, 1908, p. 1069, that it was himself who suggested this construction. He states that the gas-coolers, shown in Fig. 92, were devised by Dr Uebel, and that all this apparatus was first made by the firm of K. Oehler, at Offenbach.

time during the process. For this purpose, when mounting the set, a T-piece of glass is put in the connecting-pipe between each two receivers, the upright branch of which is as high as the receiver (Fig. 92). By simply turning this piece down, the two half-receivers in connection with it can be emptied at any time during the process, and washed out if necessary. These T-pieces also show the level of the acid at any time during the work.

7. The Cellarius receivers stand changes of temperature much better than the ordinary bottles, probably on account of the double arch by which differences of tension are equalised.

8. Their shape allows these receivers to be packed in a comparatively small space in railway tanks, ships, etc.

The results obtained with the Cellarius receivers in actual practice far surpass anything previously attained in the manufacture of muriatic acid. For each ton of common salt decomposed in twenty-seven hours twenty vessels are required, but when followed by a Lunge-Rohrmann plate-column, that number of receivers suffices for 1½ tons of salt. In three years' work Cellarius obtained an average of 190 to 194 parts "technical" muriatic acid of 32° Tw. from 100 parts of salt, calculated as 100 per cent., with a set of receivers without water-cooling, and with such strong draught that no gas blew out when the doors of the pot and of the muffle-calciner were opened at the same time. The "technical" muriatic acid contains 0·8 per cent. sulphuric acid, leaving a yield of 183 per cent. real HCl to 100 NaCl[1]

This system is also used *for cooling gases* in the manufacture of hydrochloric, nitric, or sulphurous acid, etc., for which purpose the vessels are used in an inverted position; the two gas-necks, *a*, *b*, are placed diametrically at opposite ends, so that the gases must pass upwards between the water-cooled arches under a certain pressure, and the condensed liquid runs away at *f*, as shown in Fig. 93.

Th. Meyer reports (*loc. cit.*) that the Cellarius system has been very successfully employed in the Ochler-Meyer bisulphate process (*supra*, p. 184), in both shapes just described. The gases are first cooled by an empty vessel of the shape shown in Fig. 93; they then pass a gas-filter, of the kind to be described later on, by which nearly all arsenic, iron, selenium, and sulphuric acid is retained. They go next into a preliminary set of receivers, placed in hot water, so that the gases may enter with a temperature of 150° to 180° C., and then into the proper condensing-receivers, only half of which need be cooled by water, as the temperature even in front never exceeds 80° C. Four Oehler furnaces are combined with altogether 72 receivers, of which 48 are water-cooled. At the end there is an ordinary tower, filled with cups or any other materials, but this tower has very little work to do.

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[1] *Cf.* also *Z. angew. Chem.*, 1908, p. 104.

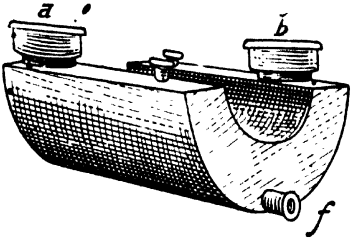

FIG. 93.

If Cellarius receivers are fitted with such an amount of water-cooling that their temperature does not exceed 15° C., pot gases can be condensed to an acid of 40° Tw. = 38 per cent. HCl, which is quite impossible in ordinary condensing plants, though such acid is required, for instance, for the manufacture of aniline hydrochloride.

Special Arrangements for Receivers

The following arrangement permits of working with ordinary Woulfe's bottles without side-branches, and yet of attaining to a great extent the advantage of systematic condensation and saving of labour:—There are two rows of bottles, as usual. The gas, however, only travels through one of them, A, in one direction, and returns to the other, B. Next day the pipe-connections are changed, and the gas is first admitted into B, *i.e.*, into that bottle which on the preceding day had been the last of all, and it then returns through the series A, which has now been filled with fresh water. This change is made every day. All the bottles of one series are filled and emptied at a time. They have each a neck at the bottom; over this a gutta-percha tube is put, which joins a main pipe running along the whole series; the latter lies in a wooden shoot, to prevent its sagging by heat, and its projecting end is ordinarily bent upwards. Thus all the bottles are connected with each other and with the main pipe. At the end of the shift, that series of bottles which has had the gas twice and consequently contains strong acid, is emptied by bending downwards the projecting end of the main pipe. Then the latter is bent upwards again, and now, if water is run into any one of the bottles, all of them are getting filled at the same time.

For condensing the pan-gas not quite so many receivers are needed as for the muffle-gas, because the former is richer in HCl and comparatively cool and moist. From 35 to 50 bottles suffice for an ordinary small pan, decomposing daily from a ton to 30 cwt. of salt. The much more dilute, hotter, and drier furnace-gases are more difficult to condense, and there ought to be 70 or 80 bottles for each muffle; and even then the gas cannot be condensed very well by these alone, nor can very strong acid be obtained from it. Sometimes, on the contrary, a larger number of receivers are employed for the pan than for the muffle. In order to fix the last portions of the acid, which are not retained by water alone in receivers, Kuhlmann employed *milk-of-lime*, poured over coke in a special apparatus, and thus offering a large surface to the current of gas.[1] He did this in stoneware bottles also, but with a very large mouth, closed by a lid and a water lute, to which at the same time a funnel for running the milk-of-lime was attached. The vessel is filled through the mouth with lumps of coke about the size of a fist. The liquid runs about half-way up the bottle, the upper half of which is therefore filled with coke alone and exposed to the gas. The milk-of-lime, continually running in from a higher reservoir, runs off below as calcium chloride. The pan-gas of a furnace decomposing 266 kg. salt with 279 kg. sulphuric acid of 58° to 60° Baumé (in what length of time?) first passes through 66 ordinary bottles, then through 6 lime-bottles of the sort just described—that of the roaster through 36 ordinary bottles, then through 4 lime-bottles, and ultimately through a flue filled with quicklime, several metres long, before reaching the chimney.

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[1] Kuhlmann is usually quoted as the inventor of the arrangement described in the text, which certainly was first (and perhaps exclusively) at work in his factories; it was not he, however, but Marsilly, who first proposed this arrangement, when the inhabitants of Amiens complained of the vapours escaping from Kuhlmann's works; and the latter was compelled by the authorities to adopt it (*Annales des Mines*, vi. (5) p. 100).

This process, employed for some time at Kuhlmann's works, is not to be recommended; and it is inconceivable how, so long after the introduction of Gossage's coke-towers, it could have been proposed, and even commended by some. The whole arrangement is very complicated, exposed to constant disturbances, can only act imperfectly (on account of the low fall of the milk-of-lime), and involves the loss of all the lime. The Belgian Commission (*cf.* p. 68 of their Report) carefully investigated this plan, and rejected it as quite useless. Even when the lime was constantly stirred up, which on the large scale would not be practicable in this apparatus, a large quantity of uncondensed HCl passed through, and the Belgian factories consequently found themselves compelled to give up the process again. Afterwards Kuhlmann himself replaced the lime by natural *barium carbonate*, in order to utilise the barium chloride for the manufacture of permanent white ($BaSO_4$). At his factory at Roche-les-Amiens there were for each decomposing-furnace 160 receivers, 30 of which contain barium carbonate. Ultimately the gases enter a mechanical washer, viz., a cistern covered with a wooden lid, in which an agitator causes a continuous spray of water, holding finely ground barium carbonate in suspension. From 100 parts of 92-per-cent. salt, 20 parts of acid is said to be obtained as barium chloride, in addition to 140 parts of hydrochloric acid (34° to 36° Tw.). Even this second method (which, according to Stas's report, affords almost perfect condensation) cannot be recommended from a technical point of view. It utilises a material obtainable only in restricted quantities, and produces a by-product only saleable to a very limited extent. Moreover, it is much simpler and cheaper to decompose the barium carbonate, without grinding it finely, in special apparatus by means of the dilute acid which might be obtained by a coke-tower placed behind the receivers. It is not even necessary to make any weak acid at all: all the water can be run on to the tower, and from this into the first receiver, so as to be ultimately discharged as strong acid.

Another half-measure, and consequently unsuitable, is the use of the "cascade-bottles," sometimes placed at the end of the series, provided with a wide central opening, in which a perforated funnel filled with coke is introduced, and water run down the same; for of course the gas does not pass *through* the funnel, but only *round* it, and the whole complicated arrangement does very little good

Concluding Remarks on Condensation by Woulfe's Bottles.

It may be assumed that for each 100 kg. salt 140 to 146 litres of water must be run through the receivers, if strong acid is made exclusively In practice, where much weak acid is made in the last washing of the gas, perhaps twice as much water is used.

Condensation by Woulfe's bottles (touries) *alone* is only suitable for small or medium-sized works, especially if strong and pure acid is aimed at; even then it can be replaced by a combination of stone tanks and coke-towers. For the same quantity of salt decomposed, bottles sufficient for condensing all the HCl are sometimes more costly in large works than coke-towers, they require much more space and supervision, and are often very troublesome through frequent breakages of bottles. This holds good less of pan-receivers than of muffle-receivers; everything of course depends upon the quality of the ware. Long series of bottles check the draught very much, without affording a sufficient equivalent for it, as coke-towers do, where the increased friction goes hand in hand with an increase of condensing-surface. The advantage of better cooling, which bottles have against the larger stone tanks, is to some extent counterbalanced by the multiplication of apparatus and of joints.

The principal drawback of bottles, when employed by *themselves* (and not merely as accessory to coke-towers), is that the liquid and the gas have comparatively few points of contact with each other. If on cementing the arms in the bottle-necks a little tar-cement has got inside, the thin oily layer forming on the liquid prevents contact completely, and the bottle in question ceases to work: this can be ascertained by its remaining cold. Bottle-receivers by themselves consequently are not to be recommended; but combined with coke-towers of considerable size and made of the very best material, as will be described hereafter, they are adapted for all but the very largest works, in which, in the English fashion, each pan is intended to accomplish its maximum of work.

For small works a combination of Woulfe's bottles with packed absorption towers can be made very effective.

Coke-towers.

The most important advance in the condensation of hydrochloric acid was the introduction of the *coke-tower*, invented by Gossage in 1836. This is a tower- or column-shaped apparatus of stone, brickwork, or stoneware, filled with coke or some other porous material, over which a continuous rain of water trickles, whilst the gas from which the HCl is to be removed passes likewise through the tower, best in an upward direction—that is, opposite to the current of water. Gossage himself, as can be seen from his *History of the Soda-Manufacture*, p. 27, derived no pecuniary advantage from the general adoption of his invention, but, on the contrary, suffered the loss caused by the first costly experiments.

Coke-towers are now the principal condensing-apparatus in most of the larger alkali-works. Their action is based upon the following facts (very clearly pointed out by Dr A. Smith):—When the air contains but very little HCl (say 0·003 per cent.), it appears cloudy in damp weather. Even when it has been condensed in a rapid current through well-cooled pipes, it still appears cloudy on leaving them; but when it has been passed through small pieces of coke or through very narrow damp channels, it issues clear. The floating acid particles which are too small to be precipitated seem to be retained like precipitates on a paper filter. The essential point is therefore the surface-contact. Few materials offer such a large external and internal surface as coke. Its inner surface, enormous as it is, is not directly utilised, since the pores are filled with liquid acid and do not allow the gas to pass. Stones or bricks would therefore seem to afford the same action, but the pores of coke act indirectly by the continuous diffusion of acid from within and fresh water from without. Some factories, indeed, employ firebricks or specially moulded fireclay lumps with many perforations (see below). Sometimes with open roasters bricks are employed in the lower and coke in the upper part of the condensers. Still, for the sake of simplicity, we sometimes call all these apparatus "coke-towers" or, generally, "condensers." The object of employing bricks is partly to afford wider spaces in cases where any soot might be deposited, partly to avoid ignition of the coke by hot gases from open driers.

Coke-towers are usually of square section, occupying 9 to 64 sq. ft. of ground-space, and 5 to 120 ft. high. They are employed either single or several together, and communicate either with the open air or with a chimney. Of course these conditions are not arbitrary, but are determined by circumstances, such as the size of the batches, the kind of roaster, etc. But as the gas always issues very hot, especially from the roasters, cooling it by long conduits is of great advantage; otherwise the condensers themselves get very hot. If it is sought to remedy this by running down very much water, a dilute acid is obtained, and the passage of the gas may even be obstructed too much.

The furnace-gases cannot be completely condensed in a single tower, if strong acid is to be made. The gas is therefore allowed to pass through a flushing-tower or *post-condenser*, where it is washed with a good deal of water, whilst the resulting very weak acid is run to waste, unless it is pumped up for feeding the condenser proper. The pan-gas by itself can be condensed by a single tall coke-tower not connected with a chimney.

Post-condensers are generally considered an evil, to be avoided if possible In England the tendency has been for some years to make the main condensers very wide and high, and to do without any post-condensers, not merely for the pans, but also for close roasters; in open roasters this is not possible. But this simplification is not without its drawbacks. We see from the *Alkali Reports for* 1884, p. 87, that at a very well-managed factory some furnaces worked with a post-condenser for every two main condensers, and other furnaces without any post-condensers The former condensers furnish acid of 26° Tw., but the latter cannot be run stronger than 22° Tw., as otherwise there is danger of exceeding the legal maximum of escape of HCl in the acid-gas. At that factory the weak acid from the post-condensers is employed for feeding the main condensers, and this is now the general plan.

Condensers, according to Dr A. Smith, may have the following defects:—If the coke is *too loosely packed* or the pieces are too large, there is not enough surface opposed to the gas; the layers easily collapse, form compact masses, and allow the gas to pass more easily through another part of the sectional area. In this case a large portion of the tower remains inactive, and consequently the really efficient portion of some very large condensers is very small. Exactly the same thing happens when the coke is *packed too tightly*. In this case so much resistance is offered to the gas that it seeks the wider passages, never entirely absent. A very bad case is that of condensers getting *out of plumb*. Then the water does not run down equally, and the gas of course principally ascends on the dry side, where it meets with less resistance. Thus a large tower fed with much water, may become worthless, as actually happened in a Tyneside factory. There this was partly remedied by putting in wooden shelves on the overhanging side, which compelled the water to flow across to the other side of the tower. Very frequently the condensers are *too small*. This can be counterbalanced by a larger feed of water, but only to a certain degree. A certain time is required for condensation, and if the condensers are not high enough, the largest supply of water cannot make up for this. A large condenser consequently always works better than a small one. Cases have occurred where a strong current of water ran down and arrived only faintly acid at the bottom, whilst the gas escaped strongly acid at the top. If too much water runs down, the surface of the coke is even lessened and its efficiency impaired. The arrangements for *dividing the water* before it runs on to the coke are also often very imperfect. It is very important that the gas should always travel in the opposite direction to the water—that is, always *upwards*. Condensers with an internal partition, in which the gas first goes upwards in one compartment and downward in the other, are faulty. The first Report of the Inspector on the Alkali Act mentions a very telling case, in which such an inefficient condenser was at once cured when the gas was taken from the top downwards by a string of pipes and made to ascend in the second compartment as well.

The *draught* through the condensers should not be too strong; if the gas is pulled through too fast, condensation cannot be perfect. This does not easily happen with condensers open at the top, which, however, can only be used for pan-acid. For condensing the roaster-acid, or both together, especially for open roasters, more draught is required, and the condensers must be connected with a high chimney. At a Tyneside works the condensers situated nearest to the chimney, and exposed to the strongest draught, condense much worse than those more distant. Suitable dampers ought to be sufficient for correcting this fault.

It is sometimes assumed in England that the difference of temperature between top and bottom of a large coke-condenser ought not to be less than 50°, but in practice there is no such rule.

High condensers act like chimneys, and this once caused a very serious accident. At the Friar's Goose Chemical Works near Newcastle-on-Tyne there were six condensers 75 ft. high. On Sunday evening, 26th July 1891, one of these caught fire. It collapsed, and brought down with it three other condensers. Seven men were killed. These condensers were connected with Deacon's plus-pressure furnaces, and the accident was evidently occasioned in this way:—A crack in the bottom of the muffle, imperfectly repaired, caused the condenser to aspirate hot air and fire-gases from the fire-flues. During the stoppage of work since Saturday midnight the coke had become dry and eventually caught fire. In order to prevent a similar accident in future, a special cut-off damper has been placed between the muffle and the coke-tower at all works of the United Alkali Company.

Very large condensers cannot be made of square section, because it is impossible to get sufficiently large stone slabs. They are made hexagonal or octagonal, and are in Lancashire always built on the system shown on p. 266, but, of course, the joints of the slabs are not dressed to an angle of 45°, but to that corresponding to a hexagon or octagon. The corner brackets must also be shaped accordingly exactly as shown in Fig. 84, p. 267, in connection with the construction of the bottoms of such towers.

Perhaps the largest condenser in the world was erected at the Runcorn Soap and Alkali Works, about which Lunge received the following information on visiting the works:—The octagonal tower is 66 ft. high above the foundation. It receives the gas both from the pans and roasters of saltcake-furnaces decomposing 50 tons of salt in twenty-seven hours. The packing consists of the hardest oven-coke, carefully picked and put in by hand. The feeding-water is run from a circular tank by oscillating troughs and water-lutes. There is no previous cooling of the gas, no cisterns, no post-condensers. The gas arrives at 104°; it is considerably cooled down in the 6-ft. space at the bottom below the grate, and here much steam is formed which greatly aids the condensation. The temperature of the acid running out is 61°, its average strength = 23° Tw. The exit-gas contains on the average 0·45 grain HCl per cubic foot.

The *Alkali Works Report for* 1887, p. 45, mentions three works where similar large condensers were erected in that year alone. One of these replaced six of the ordinary Lancashire condensers, 6 x 6 x 50 ft., by two octagonal towers, 62½ ft. high, 17½ ft. wide, holding together 28,500 cub. ft., against only 11,000 ft. of the six old condensers. The former contents correspond to 200 cub. ft. for each ton of salt decomposed per week, that is the largest condensing space ever provided in Lancashire.

The interposition of *stone cisterns* between the furnaces and condensers is not absolutely necessary; even without them, complete condensation and moderately strong acid can be obtained. Still they are very much to be recommended, especially where much strong acid is required for sale. With towers alone the acid can be made sufficiently strong for own use (say 28°), but cannot easily be brought up to 34° or 36° Tw., as required for sale, unless a very large quantity of worthless weak acid is made. Of course, by lessening the supply of water to the main condenser, stronger acid will be obtained; but then more gas will pass over into the post-condenser, where it has to be condensed into weak acid. Practice has shown that with properly constructed condensers *without* stone cisterns the acid need not be below 28° Tw., but it cannot well be made stronger without incurring the inconvenience just mentioned. This is probably caused by the fact that the greatest strength can be only obtained when the acid is at rest, not falling down in drops.

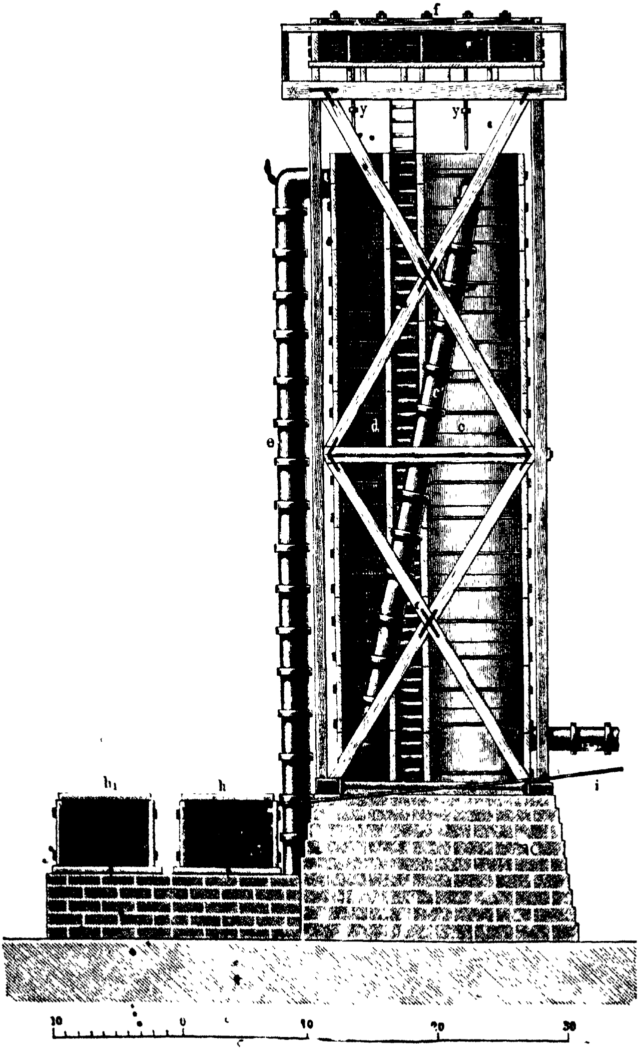

FIG. 94.

The number of stone cisterns is usually three, which is sufficient for most purposes; but sometimes six or more are employed. In the first of these most of the sulphuric acid carried along with the HCl is condensed; the acid contained in this tank is consequently impure, and that of the two following ones much purer. This, however, only holds good of pan-acid; roaster-acid can never be obtained free from sulphuric acid, because this is partly present in the furnace gas as anhydride, which is very difficult to condense completely. When there are several tanks they can be connected, and a stream of water or dilute acid may be run in them in the direction opposite to that of the current of gas, just as is done in the stoneware receivers; but the tanks are simpler, last longer, and the gas-pipes can be made much larger than with Woulfe's bottles. They have also a larger condensing surface.

Fig. 94 is a sketch of a condensing-plant sufficient for the complete condensation of the gas from two English blind roasters producing 80 tons of saltcake per week. At *a* are the pipes conveying the gas from the furnaces. They must rise high enough to have a fall of ½ in. to the foot down to the first tank, *b*. The gas issues from the furnaces in 15-in. pipes, which either enter separately into the cistern *b*, or are united beforehand by a Y-pipe; the common pipe carrying them onward should have 21 in. diameter.

It is preferable to introduce the two 15-in. pipes separately,

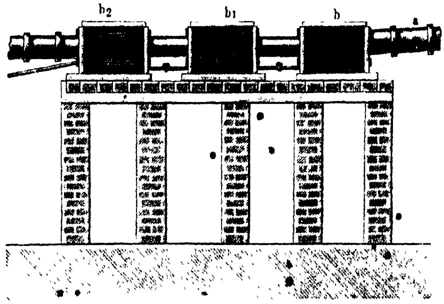

FIG. 94 (*cont.*).

because one of them can easily be stopped when either of the furnaces has to stand still for repairs. The three stone cisterns *b*, b_1, and b_2, are connected at the bottom by 1- or 2-in. stoneware pipes; and each of them is provided with an outlet-cock. The pipe *i* connects them with the stock-cisterns, *h* and h_1, and allows either all the acid condensed in *b*, b_1, and b_2 to run into them, or perhaps only that of *b*, for bleaching-powder making, whilst the purer acid from b_1 and b_2 can be drawn off into carboys for sale.

The cisterns should be placed so that the gas will rise from them to the first coke-tower—best of all, so low that the tower-acid can run into them; but there should be a fall to the store-tanks as well. The latter case is not provided for in the drawing, which of course must be modified in each factory according to the given conditions of level. The gas then enters a coke-tower, *c*, 7 ft. square and 45 ft. high; from this it is taken down in the 21-in. pipes *c′*, and enters the post-condenser *d*, which is also 45 ft. high, but only 4 ft. square. From this it issues at the top and descends through *e* downwards into a flue leading to the chimney. In this there must be a suitable damper, made of slate or rough plate-glass, etc., and never opened wider than is absolutely necessary.

It would be of course much simpler to connect the towers *c* and *d* at the top; the gas would then ascend through *c* and descend through *d*; the two strings of pipes *c′* and *e* would thus be saved. But this saving amounts to very little in comparison with the much more perfect condensing effect of the arrangement as first described.

The two towers are fed with water from the wooden cistern *f*, which is fixed on a scaffold over the towers, so that there is space for a man to stand between the top of the tower and the bottom of the cisterns. The cocks *y y* supply the water, in a manner to be described in detail later on.

The condensed acid is run from *c* into the cisterns *h* h_1, of which one is always filling whilst the contents of the other are being used in the chlorine-stills, etc. These cisterns ought to be placed high enough for the acid to run to the stills by itself; only in the most urgent cases ought pumping of hydrochloric acid to be resorted to (see p. 291). It is still better to make the condenser-foundations high enough for running the tower-acid into the tanks *b*, b_1, and b_2.

Erection of Stone Condensing-towers.

The first thing to be considered is the *foundation*. This can hardly be constructed too carefully—not merely because the weight of the tower, with its packing and the water-cistern, is very considerable, but also because the running-over of acid, which cannot possibly be prevented absolutely and at all times, tends to make the ground all round and the material of the foundation itself rotten, especially the mortar. Unless it is possible to go down to the rock, a firm building-ground must be procured by piling, just in the same way as for a very high factory-chimney. On the bottom of the foundation-pit first a layer of asphalt is laid, either the same kind as is used for street-pavements or a mixture of boiled-down coal-tar and sand, or else a melted mixture of pitch and brimstone, which becomes as hard as stone. Upon this the foundation proper is erected, either of quarried rubble stones, or, preferably, of hewn freestone. Either stone must be free from limestone or any other mineral soluble in hydrochloric acid. Most suitable is sandstone with siliceous cement. When freestone is used, it is not necessary to build the foundation as a solid block, but merely three strong pillars, especially that part of it which projects out of the ground, and which must be carried high enough for the acid to have a natural fall to the tanks and thence to the chlorine-stills. Supposing the latter to be Weldon stills (*i.e.*, about 12 ft. high all over) and the building-ground to be quite level, the height of the foundation from the ground to the condenser-bottom will be at least 18 ft.; 20 ft. will be better.

The *mortar*, even for the foundation, ought not to be either lime or Portland cement, but should consist of tar and sand. At the ground-level another layer of asphalt is laid down, which slopes away from the centre in all directions, so that no acid can lodge in any one place. A gutter is provided for taking away any acid running over, as well as the rain-water.

Upon the foundation is placed the *timber frame* which has to support the stone tower with the water-cistern on the top for feeding it. This frame is often employed during the building as a scaffold for hoisting up the stones.

The construction of frame usual on the Tyne is seen in Fig. 94 (p. 290). It is bound together at the foot by metal corner-brackets and screw-bolts. The uprights should be at least 9 × 9 in. thick; the diagonal stays may be weaker. When the frame has been erected, railway-plates are laid upon two opposite crown-trees, and bent up a little at each end. On these runs a bogie, carrying rails at right angles to the first, and on these is put a second bogie, carrying a winch, so that the latter can be run to any given place within the frame most easily and quickly. This travelling crane requires four men to work at the winch.

The *bottom-stone*, which is at least 12 in. thick and very heavy, is best put on to the foundation before the frame is erected; for this the crane is not required, as it can be hoisted by screw-jacks. It is often dished towards the side where the acid is to run away, or a hole is drilled for the same purpose. The remaining upright stones are provided with two shallow recesses near their upper edge; in these a cramp, attached to the winch-chain, gets a hold. In Fig. 95 it can be seen how one arm of the cramp enters into a square hole in one side of the stone, whilst the other side is pressed against by a screw passing through the other arm and by wood wedges. Thus the four stones belonging to each course are hoisted one by one by means of the crane, let down into their places, and provisionally fixed by iron and wooden stays, till the whole course has been completely bound and the joints made good; then the next course is put on, and so forth up to the top; the cover-stone is left off till the packing has been finished.

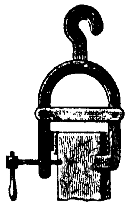

FIG. 95.

The *courses* are built just like those of the stone tanks described on pp. 262 *et seq.*, and may be constructed according to either of the two systems mentioned. Here, however, the horizontal joints between each two courses make the matter a little more complicated. For the first system, that of bevelled corner edges, an india-rubber ring of 1 in. thickness is required for the bottom, and $\frac{9}{16}$-in. or $\frac{3}{4}$-in. india-rubber cords for the upright corner-joints. These are fastened in the four corners of the bottom-ring after adapting this to its groove (p. 267), and are stretched perpendicularly up to the crown-tree; on letting down the stones care is taken that the cords get into their proper grooves. The horizontal joints are made good by strips of flannel soaked for twenty-four hours in a mixture of boiled linseed oil, red lead (two parts), and finely ground sulphate of barytes (three parts). The latter is added to retard the hardening of the cement. For post-condensers, only the bottom course below the grating need have india-rubber cord for the corner-joints; in the rest of the courses all the joints can be made good by soaked flannel strips. The upper and lower edges of all the stones must have a slight slope inwards, say 1 in., as seen in Fig. 96; in this way no acid can run out. All the edges of the stones must be well cleaned by means of a brush, as any small pebbles or rough sand would spoil the joint and do great harm. The necessary binding by means of corner-brackets and screw-bolts is very troublesome, as each single part must be supported until the last nut has been screwed home. Along with the tower a light wooden scaffold must rise up inside, upon which the men may stand.

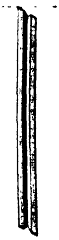

FIG. 96.

With the second system (p. 264) the erection is easier, because the stones grasp one another, and the binding especially can be done without any trouble whatever. This advantage is even more important here than for acid-tanks and chlorine-stills. On the other hand, it is less easy and reliable to make the joints good, the horizontal ones especially, because the least carelessness of the man stemming in the "black stuff" does great mischief. For this reason the following very cheap and more reliable way of making the joints is sometimes employed:—A V-shaped groove is worked all round the edges of each stone—similarly as in Figs. 81 and 82 (p. 265), if the upper and lower edges are made alike, except the slight inward bevel given to the horizontal edges. The side elevation, Fig. 96, will make this quite clear. In this way a lozenge-shaped channel is formed wherever two stones touch. As soon as a course is finished, melted sulphur is poured into all the upper openings of the channels; it naturally also runs into the horizontal channels, and affords perfect security against any leakage of acid or gas. The stones, just as when joining them by tar-and-fireclay cement, must be perfectly dry; if necessary, they are dried and gently warmed by means of a fire of shavings. Of course the sulphur would melt if the gas entered the tower much above 112° C., but that ought never to happen. A tower built in this way should not be exposed to much shaking.

Formerly sometimes the horizontal edges were made to overlap (see Fig. 97), leaving a space for putting in the tar and fireclay cement, but the system just described is preferable.

The four stones forming each course are not all made of the same height, but the sides of the first course are made a foot higher than the ends. In the next course the stones are made of equal height, but at different levels, as shown in the sketch, Fig. 98, and also in Fig. 94. Thus a much better bond is obtained than with joints running all round. This does not affect the sulphur-joints, nor the cutting of the stones, as will easily be perceived. But care has to be taken to place the iron binders always in the best way for making the bond a strong one.

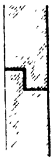
FIG. 97.

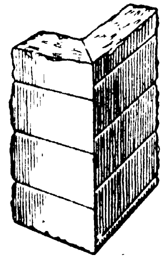
FIG. 98.

Formerly the courses were made of equal height, but the sides and ends were changed alternately from course to course.

In order to equalise the pressure of the screw-bolts upon the condenser-sides, 6-in. timbers are carried up the whole height of the tower. Sometimes these are made stronger, so as to carry the water-cistern. These timbers are not shown in Fig. 94, in four corners, so that all the screw-bolts pass through them, as seen on the plan, Fig. 99.

The stones near the bottom should be 5 to 7 in. thick, higher up only 4½ in., if very good sandstone is available. They are frequently made thicker, especially if the stone is rather soft.

The *iron parts* of the condensers must, of course, be well tarred. This must be repeated from time to time, at least twice a year, as should also the tar-coating of all the stonework or brickwork. In spite of this, bracing-rods, etc., are frequently corroded and spoilt by acid oozing out or even by rain-water absorbing some acid when dropping upon them. This is especially dangerous in the bevelled-corner system, for here the corrosion of a single screw-bolt means the destruction of the whole binding all round; and if by chance both the bindings belonging to a course were similarly spoilt, this course, and with it the whole superjacent portion of the tower, would collapse like a house of cards. In the second system, with grooved joints,

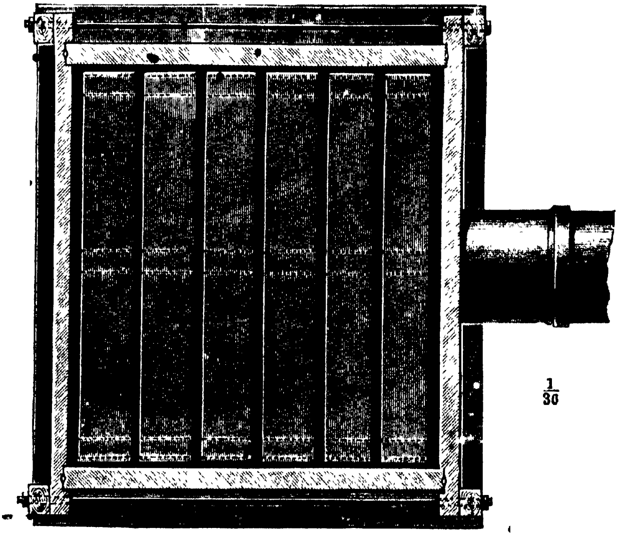

Fig. 99.

this danger is nothing like so great; but here also the corrosion of the rods is a serious evil. Sometimes, therefore, all rods, after being well tarred, are further protected by india-rubber pipes, or more cheaply by earthenware pipes put on in building, before the rod has been pulled through the hole of the second stone. A lead coating over the pipes also lasts a long time.

Now and then towers are built dispensing with iron binders altogether. In each course two opposite stones project above the next lower course, and take hold of it by recesses fitting on to two stones at right angles to themselves, so that the whole is well kept together; Fig. 100 will make this clearer. Whatever is saved here in iron, is more than counterbalanced by the extra cost of stones and labour, but there is absolutely no need for repairs, and such a tower should, as it were, last for ever. This construction is therefore to be recommended.

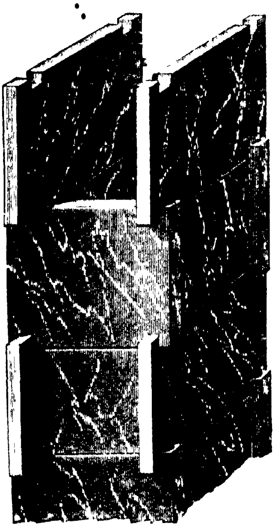

FIG. 100

Brick Condensers.

In many cases (formerly much more frequently than now) *brick condensers* were employed. In well-managed factories they were very rarely used for strong acid, mostly only for weak acid or as post-condensers. They are usually cheaper than stone towers, for instance, on the Tyne, where firebricks are very cheap; but they very rarely answer all fair expectations, and one of our most experienced alkali-makers, after trying for many years, gave up the endeavour to make his brick condensers as tight as stone condensers. If freedom from constant repair work is desired, the stone condensers are to be preferred in spite of their extra cost.

For brick towers firebricks are mostly employed, because these usually (not always) resist acids better than common bricks; in Lancashire the blue Welsh bricks (p. 269) are commonly used for this purpose. Nowadays several manufacturers make a speciality of "acid-proof" bricks. They are set in tar and fireclay, with very thin joints. Sometimes there is an inner wall and an outer jacket, separated by a layer of asphalt; more frequently the walls are solid. Some works employ specially moulded bricks, having a slope of 1 in. in their length of 9 in. Then the brickwork looks, in vertical section, like Fig. 101: inside there are the sloping bricks, outside 4½ in. of plain bricks. At the bottom a whole brick would be taken for the outside. The object of the slope is self-evident, but such towers are said not to have any great advantage over those built of plain bricks. In the latter case the walls on the Tyne are made 18 in. thick up to a height of 10 ft., and 15 in. for the remainder. Three courses of bricks are laid as runners, and the fourth as binders (at right angles to the thickness of the wall). For greater stability, and also for carrying the water-cistern, there are upright 12-in. beams placed in the corners, cut out as in Fig. 102, so as to take hold of brickwork. Every 5 ft. of height, corner-brackets and binding-rods are provided. A similar kind of binding can also be employed for stone towers instead of the frame shown in Fig. 94 (p. 290). The bottom of the tower is always formed by a single stone. The condenser is painted with several coatings of tar both inside and outside.

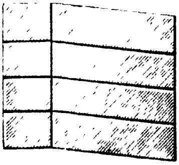

FIG. 101.

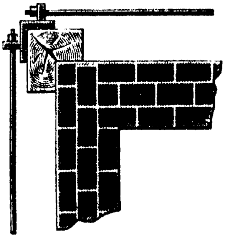

FIG. 102

Now and then condensers are built of common bricks soaked in hot tar, and immediately after walled quite hot. The weight of the bricks sets them firmly in the thickened tar, which, after cooling, solidifies and serves as mortar. If bricks previously tarred are employed, the faces to be joined should be heated and, immediately before walling, dry sand dusted upon them. This is necessary both as a protection against acid and against their sliding upon one another when the heat gets up.

In many works the post-condensers are not made as high as the strong acid condensers, but much broader, of an oblong shape, with two or three partitions, alternately open at top and bottom, so that the gas has to travel up and down. This comes to the same as three or four adjoining towers; it is not so usual with stone condensers as with brick towers.

Grating or Dome.

The construction of the *grating* or *dome* upon which the packing rests is the same for all kinds of condensers. This grating is either a pigeon-holed arch, made of the best fire-bricks, or it is made according to Fig. 103 (also above, Fig. 99, p. 297).

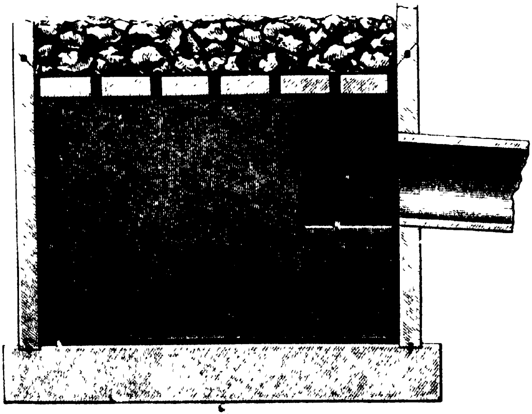

FIG. 103.

Three stone-flags are placed edgeways on the bottom-stone; they project above the entrance-pipe for the gas (say 3 ft. above the bottom), and are parallel with the gas-pipe; the middle flag is cut out in front, so that the gas is spread uniformly. The plan, Fig. 99, along with the section, Fig. 103, shows this clearly.

These flags, about 4 in. thick, carry other stones serving as grate-bars, 12 in. broad, 4 to 6 in. thick, and 2½ in. apart. In the case of very high towers, a second, sometimes even a third, grating or dome is built-in higher up, so as to lessen the pressure of the packing upon the lower parts.

If the dome has to be arched, first two dry 9-in. firebrick walls are carried up 3 ft. along the two sides of the tower at right angles to the gas-pipe; upon these a number of 9-in. arches are sprung in a semicircle from one side of the tower to the other, so as to throw the pressure downwards and keep it off the sides. These arches are half a brick wide and distant from each other by the same width (4½ in.); they are connected by special binding-bricks, which pass from one arch to the other, a distance of 12 in. from centre to centre (measured on the top of the arch), and form a continuous course; thus pigeon-holes are formed in the dome. The closers are, in the centre, 9 in. wide, in order to reach from centre to centre of two arches; the end closers must be 12 in. wide and 9 in. high, and their other dimension is 3½ in. at the top and 1⅛ in. at the bottom. The spandrels are walled up level with the crown of the arches so as to form a plane, and the whole is bound together by a wall 15 in. high and 4½ in. thick, running round all the four sides.

Packing Materials.

The *coke employed for packing* should be of the best and hardest quality of oven-coke. Gas-coke is of no use whatever here, because it is too soft and would soon be disintegrated. Immediately above the grating the largest and longest pieces are placed regularly in parallel courses, the first crossing the grate-bars, the second at right angles with the first, and so on. For each following course smaller pieces are taken, so that the size of the pieces changes from 5 to 6 in. in bottom layer down to 2 in. in the top layer. Since the efficiency of a condenser essentially depends upon the uniform distribution of water and gas in it, too much care cannot be spent on selecting and arranging the packing. It should be done by a thoroughly trustworthy man. When one-third of the condenser has been packed in this regular way, the remaining two-thirds may be simply filled by tipping-in pieces of coke, separated from all smalls by a riddle with 2-in. meshes. The coke is filled in up to the lower side of the gas exit-pipe, but after some time the packing settles down a few inches.

At first the coke yields up a little iron and organic substance to the acid; afterwards this ceases. After some years the coke-packing must be renewed, the necessity for which is indicated by the draught getting bad.

The large octagonal or hexagonal towers, in which a uniform distribution of the gases is much more difficult than in smaller towers are best packed with pieces of coke of regularly graduated sizes in such manner that the larger lumps are placed in the centre, and much smaller lumps round the edges, where the friction of the gas is greater.

In the case of high coke-towers (above 50 ft.) it is advisable to avoid the pressure of the upper layers upon the lower ones, by which the coke might be crushed, by interposing dry arches at distances of about 30 ft.; these support the weight of the superposed coke column. In this case each of the compartments thus formed can be cleaned out and repacked, if manholes are provided for that purpose. We must, however, bear in mind that the pressure of the upper column is thus converted into a lateral thrust upon those stone flags from which the intermediate arches spring, and that the ordinary construction of coke-towers is not calculated for any great lateral thrust.

Other Materials for packing Condensers.—For more than fifty years perforated fireclay blocks, or earthenware pipes, or pieces like flower-pots with perforated sides have been employed instead of coke. We shall see later that very important new systems have been developed out of this. Although so well known before, Doulton and Sanceau (B. Ps. 14766 and 14768, of 1894) patent the old system of pottery towers packed with perforated short cylinders, and perforated discs laid upon these, or tiles perforated in various ways, for the condensation of hydrochloric and nitric acid. Precisely the same thing is mentioned in the first edition of this work, and again in the second edition, *loc. cit.*

Barbier (B. P. 14014, of 1894) describes a special packing for condensing-towers, consisting of inverted cells with perforated ends, of cylindrical or truncated cone shape; a vertical central cooling-shaft supplies cold air. The perforated ends of the cells are made concave to retain any solid particles carried over.

Claus (B. P. 4108, of 1882) proposed to employ instead of coke a spongy, porous, but acid-proof material, prepared by combining silica in the shape of ganister or kieselguhr with a silicate containing more than one base. The main objection to this proposal is that the material is more costly and lasts little better than good coke.

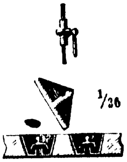

FIG. 104

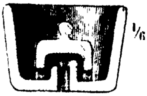

FIG. 105.

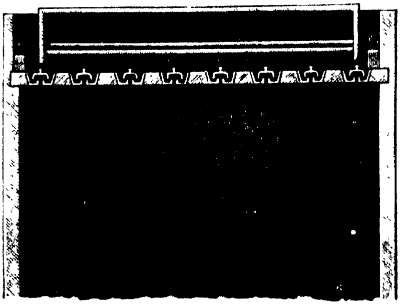

FIG. 106.

Cover and Distributing Apparatus for the Water.

After putting in the packing it is time to put on the *cover of the tower*. It consists of one or two stone flags, 3 in. thick, in which a number of holes (say sixty-four for the large condenser and nine for the post-condenser) are made, tapering below and serving for the water-lutes, Figs. 104 and 105; the joints are made good with red lead. Fig. 106 shows this. The water-lutes consist of two parts—a cup with a ½-in. short open tube in the centre, and loose cover over this. The whole top is surrounded by a stone edge 8 to 12 in. high, and the wooden oscillating bucket (see Fig. 104) fixed upon it. When this has poured its contents over one-half of the lutes, they will be filled with water, of which all that stands above the small central tube runs off directly. The nicks of the small covers allow the water to run in without letting out any gas, as there is still a shallow water-lute left. This periodical running over is very efficient for drenching the coke uniformly. As soon as the other half of the oscillating trough is filled, it turns over again and drenches the other half of the lutes.

This arrangement of oscillating trough and water-lutes is very much to be recommended, much more than simple holes in the top covers, which easily allow gas to get out. A simpler plan is to place in the hole a short bit of rope with a knot at the upper end. Sometimes the water is run into the condenser by a single swan-necked pipe, on to a splashing-plate 2 or 3 ft. below, but this does not act anything like so perfectly as the arrangement described above.

It is hardly necessary to say that instead of the simple oscillating trough (which is found even now at some large factories), more complicated and efficient feeding-arrangements can be employed, such as reaction wheels or preferably immovable overflow-arrangements. These are described with all details in *Sulphuric Acid*, to which we must refer the reader.

Raulin (special communication) has invented a distributing-apparatus which is worthy of attention, especially in cases where intermittent feeding is preferred. The following gives an idea of his system in a practicable shape:—Fig. 107 shows at A a small vessel, with a narrow siphon, *b*, which fills even with a very slight feed from tap *a*, and discharges the contents of A at regular intervals into vessel B. This vessel having been filled (if the difference in the width of pipes be not too great), siphon *c* will begin to run, of course at greater intervals than *b*. This operation can be made more exact by making the outer limb narrower than the inner, as shown in the figure. The same principle is continued by further vessels and siphons, with increasing quantity and decreasing frequency of play of the siphons. According to Raulin, the following is a suitable graduation:—The outlet of the siphon in the first vessel A ought to be 0·16 in.; the siphon in the second vessel, B, should be at least 10 in. long and have an outlet of at most 0·4 in. wide; that in the third vessel, 16 in. long and at most 0·8 in. in width of outlet; in the fourth vessel, 2 ft. long and 1·2 in. width of outlet; in the fifth vessel, 3 ft. 3 in. long and

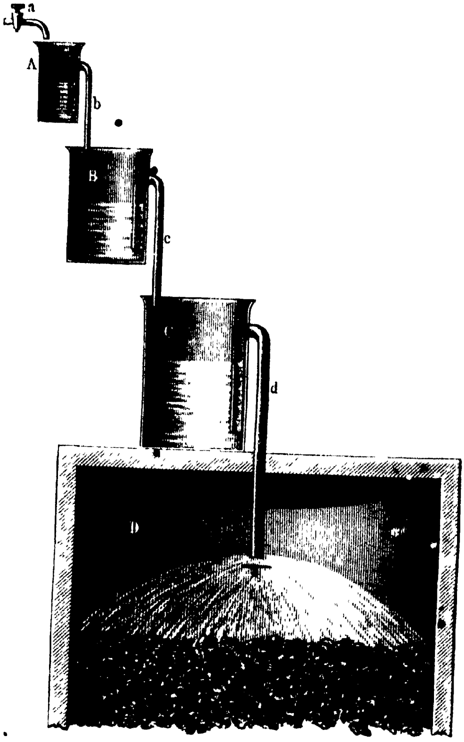

FIG. 107.

·6 in. width of outlet; in the sixth vessel, 4 ft. long and 2 in. idth of outlet. Usually two or three vessels will suffice. About n inch below the outlet, *d*, of the last vessel there is fixed a orizontal disk *e*, three times as wide as the outlet; by this the ater is made to splash about in a dome-shaped form. The iameter of this dome must correspond to the width of the tower D, and we can calculate for the radius R the necessary height H of the vessel C, with a siphon of length l and width d, by the following formula:—

$$R = 6H\sqrt{\frac{d}{l+54d}}.$$

The height of e above the surface of the coke in D must be found by experiment; it must never be more than ½H. If the pressure on the siphon be lessened, the liquid dome contracts, so that finally the whole surface of the coke is moistened in a very uniform way and at regular intervals of time.

Schuller[1] modifies the apparatus of Raulin in a very judicious way. He divides the inner limb of the siphons into two branches, one of which dips into an open cup: by means of this arrangement the siphon empties itself completely at every run, and no frothy mixture of air and water is formed. The inside diameter of the siphons is best = ½ in. The dimensions of the various vessels are planned so that for a certain setting of the tap they are all filled at the same time, *e.g.*, in eighty seconds; this can be altered at will by a different setting of the tap, and the quantity of water is easily measured in the same way. Schuller prefers as dividing-apparatus the acid-wheel with a glass bulb floating on concentrated sulphuric acid, and a bell announcing every revolution, to the fixed overflow apparatus and splash-plates.

Klute & Ising (Ger. P. 209276) describe an apparatus for the automatic and uniform feeding of absorbing- and reaction-towers, consisting of several running-off pipes, arranged in the casing of the float, each of them provided with a valve, so that in the case of changes in the feeding-liquid one or more of them are entirely shut or opened, thus preventing any changes of the feed by the fortuitous stopping-up of the exit-pipe.

Running-off the Condensed Acid.

The *condensed strong acid* runs off through a 1½ in. earthenware cock just above the bottom of the condenser, and is carried to the stock-cisterns, which should hold twenty-four hours' make. The weak acid from the post-condenser is either run away, or used for some special purpose or pumped back for use in the strong-acid condensers.

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[1] *Z. angew. Chem.*, 1895, p. 373.

Coke-towers combined with Tanks.

The connection between the tower and the tanks may, for instance, be made in the way shown in Fig. 108 (from Schrader[1]). A is the foundation, B the lower part of the tower; *r r*, the grates; C, space for the gas and the liquid acid, which runs off through *i* into the tank D; *b*, a glass or earthenware overflow from D into E. The acid vapours, of course, take the opposite direction—from E through *a* into D, and through *a* into C.

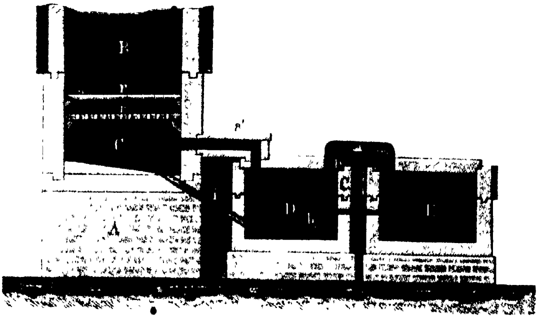

FIG. 108.

Figs. 109 and 110 give an example of coke-towers of a large works. They represent the pan-condensers at the Tyne Chemical Works, Gateshead, from the first Report on the Alkali Act. The section, Fig. 109, shows only one condenser, but for the sake of greater stability six, for as many pans, are built together, in two rows of three each, as shown in the elevation, Fig. 110. In Fig. 109 *a* is the decomposing-pan, working up 10½ cwt. per hour, or about 12 tons 16 cwt. in twenty-four hours; *b* is the string of fireclay pipes; *d d* is the coke-tower itself, 5 × 5 ft. wide inside. The height of the base is 5½ ft.; that of the stone condenser itself, 100 ft.; that of the water-cistern house, 15 ft.; and the pipe *k* for the escaping gas

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[1] *Dingl. polyt. J.*, clxx., p. 183.

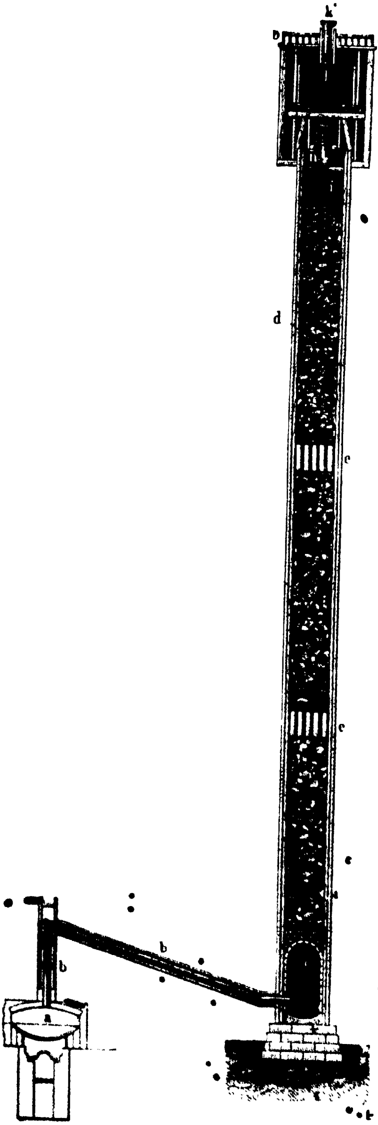

FIG. 109.

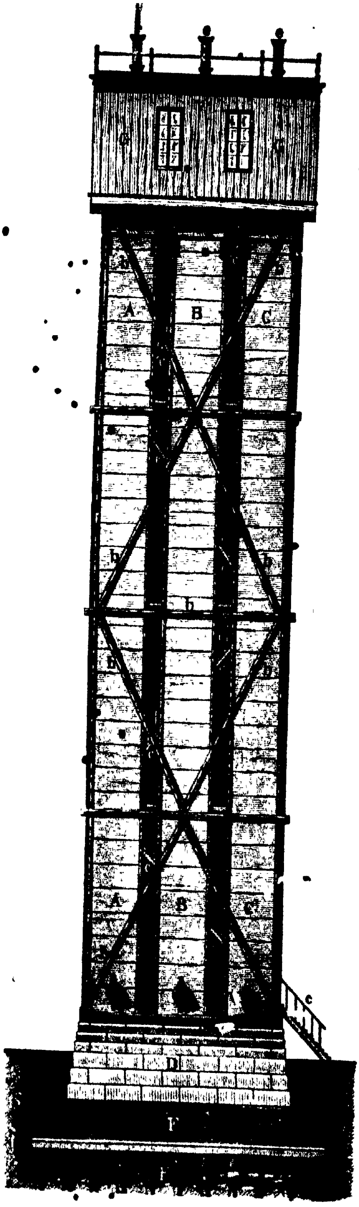

FIG. 110.

projects 3 ft. above the roof of this house. The column of coke is divided into three parts by the brick arches *e e*, to prevent the lower strata from being crushed by the weight of the upper ones: for towers of less height these arches are not required. *i* is the exit for the non-condensed gases through the pipe *k*; *l*, a water-cistern; *n*, the oscillating trough; *o*, a stage on the roof of the cistern-house for getting to the pipe *k*.

In Fig. 110, A B C are three of the condensers, D the foundation with the concrete basement E, resting upon the piles F; *a a* the mouths of the gas entrance-pipes, *b b* the stays of the timber frame, *c* the stairs, G G the cistern-house, *e e* the escape pipes for the gas.

Fig. 111 shows *condensers for open roasters, packed with bricks*, as formerly working at Messrs J. Hutchinson & Co.'s Alkali Works, Widnes, but now discontinued.

Earthenware Coke-towers.

For smaller works the best kind of condensers are those constructed of large *earthenware pipes*, combined with bottle-shaped receivers or stone cisterns. The pipes are made either of the same stoneware as the best receivers, or of fireclay, and in the latter case boiled in tar. Their joints are made with tar and china-clay. The bottom pipe stands either on a stone cistern or on a solid stone plate, in which a groove for that pipe has been cut. This groove is gently heated by a fire of shavings; the pipe is put on, leaving below it a space of about ⅛ in., small bits of slate having been put in; the joint is filled with melted asphalt; the cement is pressed in smoothly by means of a hot flat-iron; and, lastly, for greater safety, it is walled round with a ring of firebricks set in tar. In order not to allow any acid whatever to get to the joint, it is best to dish the bottom stone, and to drill a hole from the lowest point in a downwards slanting direction; into the hole thus formed an earthenware pipe for the liquid acid is introduced. The remaining large earthenware pipes are easily put on. The joints are all made with tar and china-clay. At least each third or fourth pipe should be supported from the timber frame by means of beams placed underneath its socket so that the bottom pipes need not support the weight of the whole column.

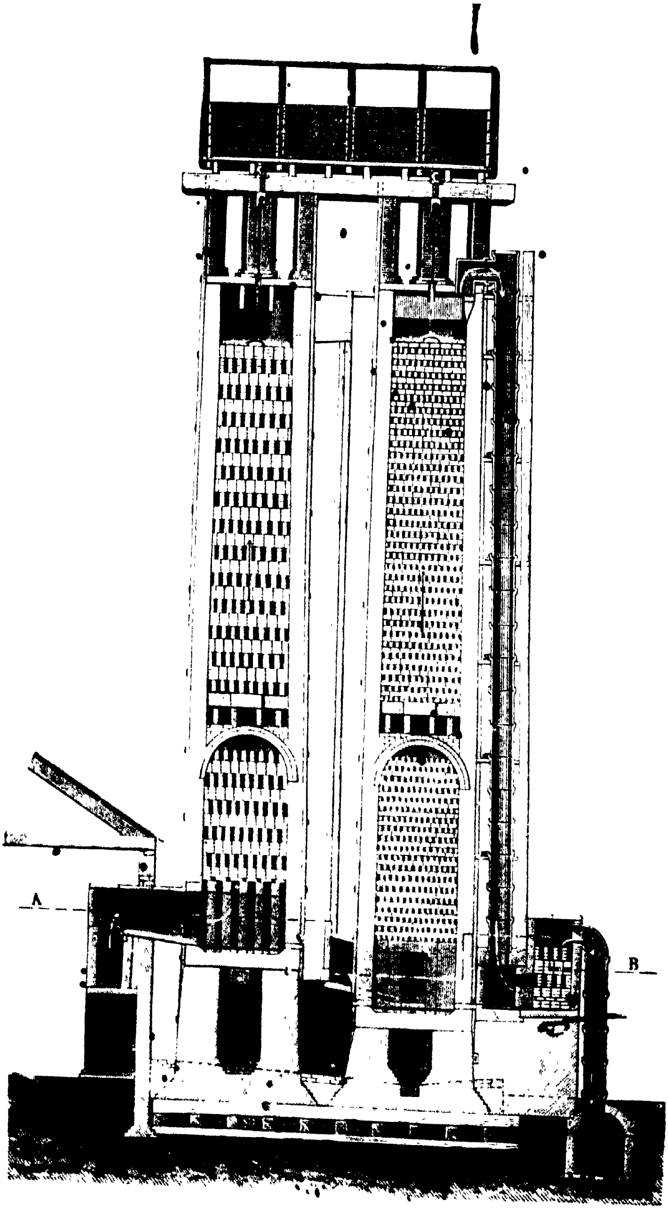

Fig. [illegible]

Since a single pipe tower, filled with coke, even of the largest practicable diameter (say 3 ft.), is unable to condense the gas from a pan working on the large scale, several such towers should be combined and the gas divided among them by branch pipes. This is done in the simplest way by conveying the gas first into a long stone tank, placed in front of the condensers, from which as many branches depart as there are pipe towers. The same cistern serves for collecting the acid and getting up its strength. Special earthenware vessels for dividing the gas may be provided, instead of the above arrangement.

Earthenware condensers are very well adapted for the gas from pans and from blind roasters, but there is some risk in employing them for open roasters, since the pipes are subject to cracking by too much heat. If this happens, one or two iron hoops are laid round the cracked pipe, consisting of two halves joined by screw-bolts. As these, if left unprotected, would soon be eaten through by acid oozing out, they are lapped round with tarred spun yarn and the whole thickly coated with tar; moreover, they are kept off the leaking place by wooden wedges. Coating the hoops with lead is also a good plan.

According to Lunge's experience such towers need only have two-thirds the area of stone condensers—no doubt partly on account of the much better cooling arising from the thinner walls and the greatly increased surface, and partly on account of the better division of the water on the much smaller area of each single pipe.

Sometimes, instead of earthenware coke-towers, apparatus similar to that shown in the first edition of this book, Vol. I., p. 378, Fig. 160, for absorbing the nitrous gas in the manufacture of sulphuric acid, are employed. In this case, within a column of earthenware pipes shelves of the same material are fixed, so that the water supplied at the top runs down very slowly, whilst the gaseous current ascends in serpentine windings. But this does not afford anything like so good a contact between gas and water as coke-towers, and the advantage claimed for this system, that the draught is less impeded by it than by coke-towers, is rather to be considered a fault (*cf.* p. 288).

Hazlehurst (B. P. 4233, of 1879) describes earthenware pipes filled with coke, 12 in. wide, into which the gas is forced by injectors made of Yorkshire flag, and condensed by water. As this patent has not been completed, its success cannot have been great.

Aussig Condensing-plant.

A number of medium and smaller alkali-works have adopted the set of hydrochloric acid condensing-apparatus introduced by Mr Schaffner at the Aussig chemical works, where the earthenware itself is also manufactured. Figs. 112 to 115 represent this system. At Aussig blind roasters are employed, making in twenty-four hours twelve batches of 8 cwt. each.

The condensing-apparatus for the pan-gas is separate from that for the roaster-gas, especially in order to obtain hydrochloric acid pretty free from sulphuric acid. Much more sulphuric acid is present in the roaster-gas than in the pan-gas, as we have seen If its presence does no harm, such a separation of condensing-plant is unnecessary

The gas from the pan, being less hot, travels through a flue made of fireclay pipes to the small tower A, Fig. 113. The hotter roaster-gas is taken first through a flue made of tarred bricks, then through fireclay pipes into the small tower B. The two towers A and B, built exactly alike, fulfil two purposes, viz :—first, cooling the gases before they get to the receivers, and, second, washing them without subjecting them to any water-pressure. They are provided with a stone grating, below which the gas enters. The whole space above the grating is filled with earthenware dishes of a special shape, which are moistened with water by a special contrivance four times a day. The sulphuric acid, having more affinity for water, is almost entirely retained here, and nearly pure HCl passes into the proper condensing-apparatus. This consists, for each pan or roaster, of 53 receivers, whose arrangement is shown in the drawings. The first double series of receivers *a* is provided with long connecting-pipes (*r r r*, Fig. 112) for the better cooling of the gases; in the second double row (*b*, Fig. 113) these long pipes are not required. From the receivers the gases pass into an earthenware tower, entering underneath a grating inside the same. The tower is two-thirds filled with earthenware dishes as above; the uppermost third contains coke. On the timber

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frame of this tower a water-cistern (R, Fig. 115) is placed, from which the water issues by means of a turbine distributor, moved by the falling water itself and spreading it all over the tower. From each tower a pipe carries the residual gases

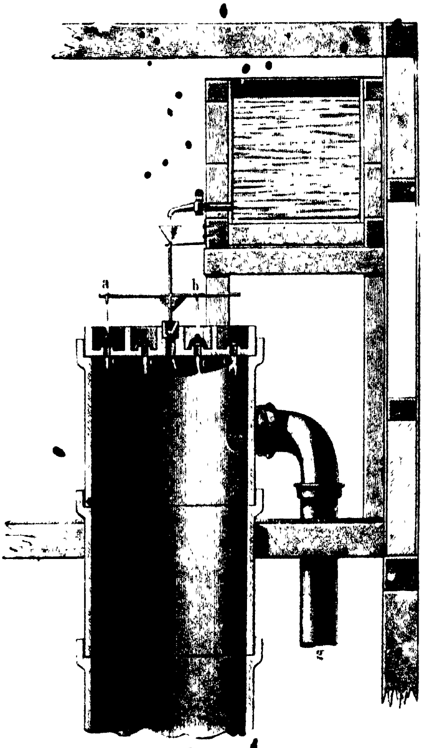

Fig. 116.

downwards, and both systems (for the pan and the roaster) ultimately unite in the large receiver P, Fig. 113; from this a pipe descends into a flue leading to the chimney.

In order to observe and examine the exit-gas continually, each system is provided with a "sight," closed by glass panes, visible in Fig. 114 at *l l*. In these at the same time the draught

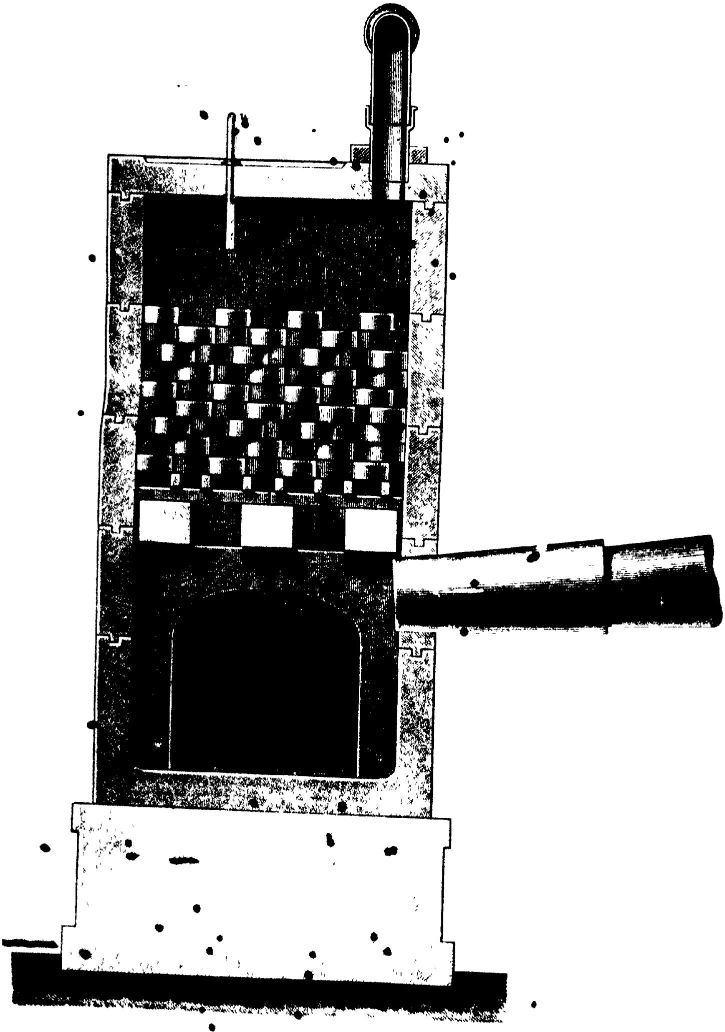

FIG. 117.

can be regulated by putting more or fewer plugs into the grating with round holes, lying in the sight.

The acid issues from the tower 12° Tw. strong, runs through all the receivers, and arrives in the first receiver 35½° Tw. strong. The acid condensing in the small towers A B is run off separately by stoneware cocks. In order to check the process, glass cylinders are interposed in several places, through which the acid runs, and in which hydrometers show the percentage of HCl.

Fig. 116 shows one of the towers in sectional elevation. The distributing-wheel empties its contents of water through *a* into the outer, through *b* into the inner compartments of the cover; *c* are glass tubes cemented in; *f*, the pipe for running off the acid; *g*, the gas exit-pipe.

Fig. 117 gives the details of the small preliminary tower. *w* is the injecting-pipe, coming from the water-main, E the entrance-pipe of the gas.

The principle represented by the "preliminary tower" (already fully described and illustrated in the first edition of this book) has also formed the substance of a patent by Hargreaves and Robinson, No. 5809, of 1882. Between the place where the hydrochloric acid is formed and the condenser they interpose a "purifier," kept at such a temperature that only the vapours of ferric chloride and sulphuric acid are condensed, with but very little hydrochloric acid.

The Deutsche Solvaywerke (Ger. P. 163371) cool the gases by means of a flush tower, passing the hot liquid which runs out at the bottom through a cooling worm and employing it over again for feeding the tower.

Wooden Coke-towers.

Such towers are employed at some French works as post-condensers. They are cylindrical in form, composed of 2 in. or 3 in. pitch-pine planks, and are held together by screw hoops, which are kept away from the wood by laths, so that any acid oozing out does not get to the iron. That the woodwork and iron should be protected by frequent painting with best tar-varnish is a matter of course. Covering the hoops with lead is still better. Even tanks for weak hydrochloric acid have been made on this principle, illustrated by Fig. 118. Some works, however, have had bad experience with such wooden towers and tanks and have discontinued using them.

A method of construction which the author has used largely for wooden vats containing acid liquors was brought to his notice by Mr George Romanes, M.I.C.E. It is equally applicable to wooden towers, and enables one to construct circular vessels of any kind without the aid of skilled coopers. The construction will be clearly seen from Figs. 119 and 120, though the bosses should be staggered and not in line as shown on the drawing. For cylindrical vessels above 4 feet in diameter, two tightening bosses should be used on opposite sides of each hoop. Ordinary steel rod of ¾ to ½ in. diameter (depending on diameter and the number of hoops) is threaded at both ends and

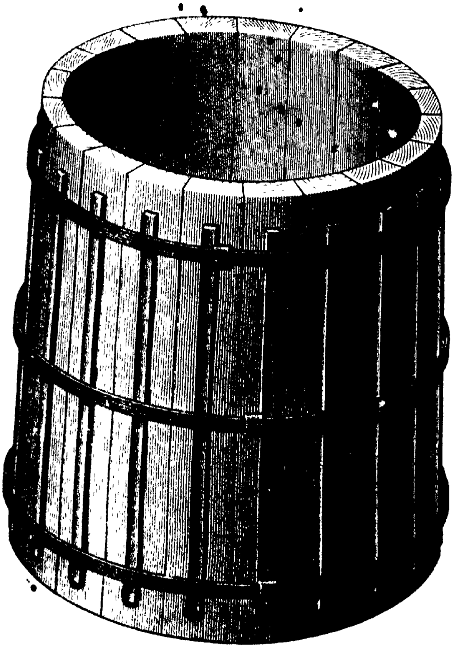

FIG. 118.

By tightening up nuts on the threaded ends, great pressure can be applied to the wooden staves and a watertight construction is readily obtained.

Size of Coke-towers.

According to the late Dr Angus Smith a condenser of 50 ft. height and 5 ft. sq. suffices for the gas given off by decomposing

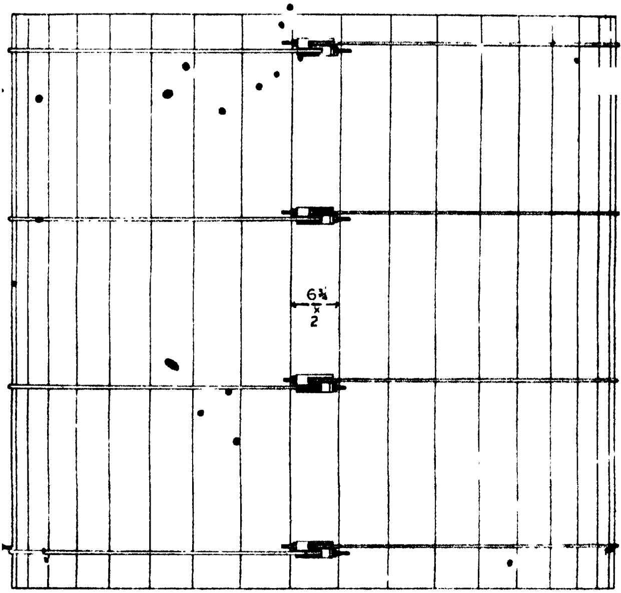

Fig. 119.

5 tons of salt in twenty-four hours, if the supply of water is properly regulated. This refers to blind roasters. Dr Smith even prefers two such condensers of equal size for the pan and roaster, but this is doubtless not absolutely necessary. It may be safely asserted that for *two* pans, if alternately worked with regularity, a condenser of 6 by 6 ft. section, and 50 ft. high is quite sufficient, especially if the gas previously passes through two or three acid-tanks, even if the two pans decompose up to 20 tons of salt in twenty-four hours. In case of need, even much

less condensing-space has been found to suffice; but then there is great danger of an escape of acid vapour at the slightest carelessness; and in any case the quantity of strong acid obtained is much smaller than it ought to be. It is, no doubt, preferable to make the tower 60 or 65 ft. high, because then more and stronger acid is got. Some works even have them 100 ft. high, but this is inconvenient and unnecessary, at any rate if acid-cisterns are employed. At one works possessing such high condensers, it was preferred in a new erection to build two towers of 50 ft each, the gas passing from the top of the first to the bottom of the second, and out of the top of this into the air. All this refers to stone condensers; earthenware coke-condensers only require two-thirds of the sectional area, but the same height (p. 309).

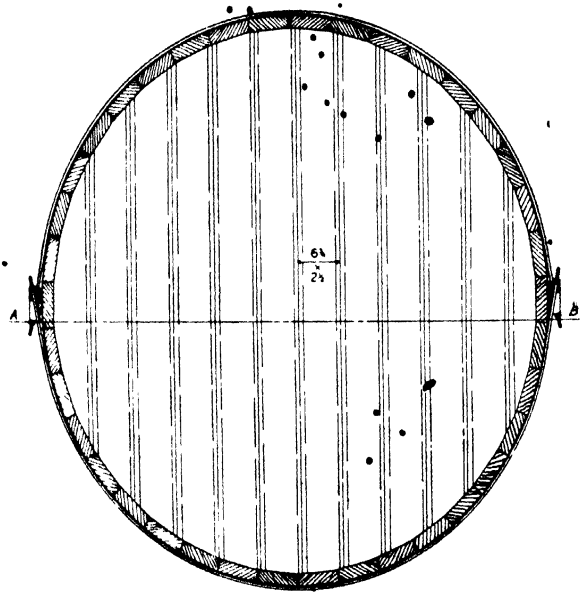

FIG. 120.

Chandelon gives the following details for Belgian factories, relating to the year 1871 and to pans and roasters together:—

	Cubic capacity of the *cooling-apparatus* for each 100 kg salt decomposed in 24 hours	Cubic capacity of the condensers themselves
	Cubic metres.	Cubic metres.
I.	0·378 to 1·480	2·400 to 3·400
II.	0·438 „ 1·001	1·373
III.	3·380 to 4·720	
IV.	0·826 „ 1·000	1·770 „ 2·080

Condensers for the gas from *open roasters*, if strong acid is to be got from them, should be as high as, but wider than, pan-condensers; if only weak acid is aimed at, they are usually made much lower (20 to 30 ft. high), but of so much the larger area. Frequently they are made of bricks (*cf.* p. 298), but better of stones—the gas being previously cooled, lest the stones should crack. Where furnace-gas has to be condensed by an excess of water, Dr Smith states that a condensing-space of 4 cub. ft. for each cwt of salt decomposed per diem is sufficient, and this is found true in practice

The dimensions of stone coke-towers at English alkali-works are best illustrated by the following table, taken from the *Alkali Inspectors' Report for* 1884, p. 82, referring to the towers then existing at the various works at Widnes. Apart from the condensing-space, we also find the average escape of HCl stated for each case. Only blind roasters are used there.

Salt decomposed per week.	Contents of the towers.	Condensing-space per ton of salt per week.	Average escape of HCl in the exit.
Tons.	Cub. ft.	Cub. ft.	Grains per cub. ft.
315	30,100	95·5	0·145
605	33,000	54·5	0·10
370	18,000	48·6	0·14
225	9,850	43·3	0·10
180	6,000	33·3	0·13
400	24,800	62·0	0·12
460	13,800	30·0	0·12
260	13,000	50·0	0·13
470	20,000	42·5	0·14
150	5,370	35·8	0·16
460	19,600	42·6	0·08
324	16,100	50·0	0·10
4219	209,620	49·7	0·122

Much larger condensing-space was provided for some of the Mactear furnaces, but the HCl going away in the exit-gases was slightly more than the average mentioned above.

The above report (p. 84) gives the following details respecting a particularly well-managed works:—The coke-towers are very carefully packed, the size of the pieces of coke decreasing from the bottom upwards in regular gradation. The top layer passes through a 1-in. sieve. Such a tower, holding 2050 cub. ft., condenses, without a post-condenser, all the gas of a saltcake-furnace decomposing 55 tons of salt per week, the gas being first cooled down to 82° by 300 ft. of pipes. Three of the eleven saltcake-furnaces possess a condensing-space of 37 cub. ft. per ton of salt per week. The other eight furnaces, which are worked for the Deacon chlorine process, require much more condensing-space. The pan-gas of these eight furnaces, equal to 293 tons of salt per week,[1] goes into the Deacon "decomposer," where half of the HCl is converted into free chlorine. For washing out the undecomposed HCl from the chlorine, each pan possesses a tower of about 2000 cub. ft., corresponding to 109 cub. ft condensing-space per ton of salt per week. For the eight blind roasters, belonging to this set and corresponding to 147 tons of salt, six towers are provided with a total capacity of 10,900 cub. ft., or 74 cub. ft. per ton of salt per week. The average condensing-space for all processes is 70 cub. ft. per ton of salt per week.

It is also stated in that report (p. 78) that of two works where the old saltcake process exists alongside of the Hargreaves process, one possesses only 37 cub. ft condensing-space for the former against 72 for the latter; the other works has 41 cub. ft. for the former and 49 for the latter (all of it per ton of salt per week). Hence at the second works there is very little difference in this respect between the two processes.

Other Condensing Methods.

In spite of the excellent results obtained in the condensation of hydrochloric acid by the coke-tower, first introduced for this purpose in 1836 by Gossage, and in spite of the fact that we can hardly conceive how the alkali industry could have reached its present enormous development without that apparatus, we cannot concede that it satisfies all requirements. From the outset we must acknowledge the drawbacks of its great expense, of the difficulty of always obtaining the proper material, and frequently also that of preparing a proper foundation for such colossal towers. Dr Angus Smith, assuredly one who has a right to be heard in this matter, says, in the *Fourteenth and Fifteenth Reports on the Alkali Acts*, p. 115:—"I have a great dislike to the great towers; they are certainly capable of holding a great deal of water and of acid, and to a certain extent of storing up condensing force, so to speak. This is their value, but they unfortunately store up heat, so that cooling is slow, whilst the surface from which the evaporation comes is large. If the condensers could be kept quite free from porosity, the latter objection would lose its weight."

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[1] The calculation is made in such way that two-thirds of the salt charged are allowed in this place as decomposed in the pans, the remaining third later on as decomposed in the roaster.

We shall now describe some inventions which have been made to replace the large coke-towers by smaller condensing-apparatus.

Plate-columns (Lunge Towers).

The apparatus bearing this name, which is intended to combine the functions of a coke-tower and those of a large number of preliminary receivers in a very small space, was invented by Lunge, and is therefore frequently styled "Lunge tower" (B. Ps. 10355, of 1886; 10037, of 1886; 6989, of 1889). Its principle is that an absolutely uniform division, both of the gas and the liquid, is attained by the peculiar construction of the "plates," with a large number of shallow basins, formed by a network of ledges, all of them perforated by holes provided with a small margin, these basins and holes being in different places in the alternate plates; moreover, by the continuous shocks of the gases against solid surfaces the condensation of the acid present in the shape of a fog, otherwise not at all easily condensed to real drops, is greatly promoted. These advantages enable us to perform with very small apparatus an amount of work for which otherwise large coke-towers or very many earthenware receivers are required. We must, however, bear in mind that, precisely because the condensation takes place in a very small space, the heat evolved is correspondingly intense, and that the gases must consequently be *cooled* as much as possible before entering the condensers. If this is properly done, experience has shown that the plate-column apparatus produces both a *complete* condensation and an excellent yield of *strong* acid (32° to 36° Tw. according to the season), of course on the supposition that the column of acid is made to meet the current of gas in a few earthenware or stone receivers.

Figs. 121 and 122 show on a scale of 1 : 50 the ground-plan and side view of a plate-column condenser as supplied by the Deutsche Ton- und Steinzeugwerke, of Charlottenburg, Berlin (successors of Ludwig Rohrmann). The plant here shown serves for condensing the acid from the decomposition of 5 tons of salt per twenty-four hours. For heavier work, say 8 or 10 tons of salt per twenty-four hours, the cooling-pipes and earthenware receivers must be made in two parallel rows, and the plate-columns must be made of greater width, as we shall see below.

The pipe-conduits *a* and *a′* convey the gases from the pan and roaster; the conduit from the roaster may also be made of stone, as shown p. 260, and this is to be especially recommended for heavy work. These pipes lead to small empty stone towers, A A′, and then to the wash-towers B B′, made of stoneware cylinders, which are either left empty or packed with broken stoneware, etc. The wash-towers are fed with just enough water to completely saturate the gases with steam, which produces a corresponding cooling effect, and to condense as much as possible of the sulphuric acid carried away from the saltcake-furnace. The temperature in A A′ remains so high that hardly any HCl is condensed if the feed is properly regulated, whilst most of the sulphuric acid is condensed and runs away at the bottom. These towers may also be fed with any dilute washings.

If it is not necessary to make specially pure acid, the pan-condensation may be simplified by omitting one of the towers A B, for instance the stone-tower A, in which case B serves both for cooling and washing. But for the roaster-condensation it is advisable to retain both towers. Here the hot gases should be decidedly cooled before entering the earthenware tower B

(which might otherwise crack), and should be completely saturated with steam, which at the same time produces a good cooling effect by the evaporation of liquid water (*cf.* pp. 240 and 241).

Now follow the strings of cooling-pipes, *b b'*. The figure shows a length of about 80 ft. of these, which is produced by carrying the pipes up and down at an angle of 65 degrees, the trestles carrying the pipes being arranged as ladders. This arrangement will, of course, be modified according to local circumstances. Where there is not enough horizontal space the pipes may be carried perpendicularly up and down, as shown in Fig. 135 (p. 334); on the other hand, where the condensers are at a greater distance, the cooling-pipes are carried in a straight row. Even then they must not be laid horizontally, but with a little fall towards the first receivers C C'. From the lowest points of the cooling-pipes *b b'* the condensed acid must be continually run away by a swan-neck pipe or similar contrivance.

For less intensive work, up to 5 tons of salt per twenty-four hours, a single string of pipes of 8 or 9 in. width is sufficient. For heavy work, up to 10 tons per diem, we must either take wider pipes (12 in.), or two rows of the narrower pipes. The latter is rather more expensive, but is preferable, both on account of the superior cooling effect and because it is not easy to make good round bends of large width, whilst angular bends are objectionable on account of the draught.

Now comes a series of six stoneware receivers, C C', of the ordinary shape, as shown Fig. 88, p. 272, with an overflow from the bottom of each bottle to the middle part of the preceding bottle. The acid coming from the plate-columns E E' runs through the bottles in an opposite direction to the current of the gas, and runs out of the first bottle full strength. Since here much HCl is condensed from the gases, and much heat is thus liberated, the connecting-pipes *c c'* are carried up high, and serve as cooling-pipes. For heavy work (above 5 tons salt per diem) we must either employ a double row of such stoneware receivers, or else larger stone cisterns).

Now follows the plate-columns E E' themselves, one each for the pan and roaster. The pan certainly gives out twice as much HCl as the roaster, but the roaster-gas is so much more dilute that here, as in all other parts of the condensing-plant, quite as much condensing-space is required for the roaster-gases. Experience has shown that a plate-column of sixty plates, 2 ft. 2 in. wide, is sufficient for the pan, and another such column for the roaster, up to a decomposition of 5 tons salt per diem. This means a column 16 ft. 6 in. high over all. Where more salt is decomposed, wider columns must be employed. The largest plates now made (2 ft. 8 in. diameter) will suffice up to 10 tons of salt per day. The holes in the lower plates are made 7 mm., those in the top plates 6 mm. wide.

The feeding of the plate-columns is regulated in such manner that on the one hand *all* the HCl is condensed, and on the other the acid comes out sufficiently strong. As a rule, if it issues from the columns at 25° to 28° Tw., it will come up to 32° or 36° in the receivers C C′ or cisterns. This will take place, together with complete condensation, if the plate-columns do not get hotter than 50° or 60° C., which is easily attained with the cooling-plant described. In countries where in summer the columns become hotter than that, they may be cooled from without by running water over them, taking care to prevent cracking of the cylinders composing the shell by incautious work.

The cylinders might, of course, crack even without such external water-cooling, if the gases are not sufficiently cooled beforehand. In order to prevent any trouble on account of such cracking, each cylinder ought to be strengthened by two iron hoops, covered with lead or carefully tarred spun-yarn, or else they may be surrounded with copper-wire netting, afterwards covered with tar-asphalt, as proposed by Mr Rohrmann.

Behind the plate-columns we must have some contrivance for catching the acid mechanically carried away by the draught. This can be done, for instance, by a 6-ft. column of coke put on the top of the plate-column itself. But as this somewhat interferes with the draught, owing to the small width of the column, we may employ a large stoneware bottle, F F′, placed in the conduit *f f′* leading from the columns to the chimney-flue. The "sight" *g*, which serves for sampling the exit-gas, is best placed behind the last receiver (not in front of it, as shown in the figure).

Nahnsen (Ger. P. 63036) describes a form of plate slightly differing from the above.

Practical Results obtained with Plate-towers.—Mr G. Lasche, manager of a large German alkali-works (Messrs E. Matthes & Weber, of Duisburg), has made a detailed report on the plate-towers erected there, of which the following is an extract, together with Dr Lunge's comments.

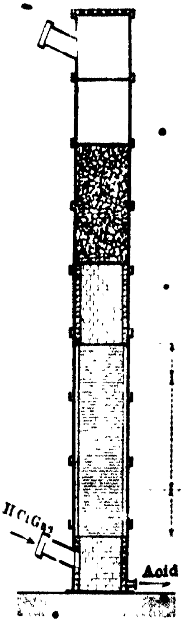

Fig. 123.

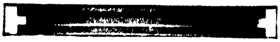

Fig. 124.

The saltcake furnaces at that works decompose, per twenty-four hours, ten charges, together 4 tons 5 cwt. rock-salt (= 30 tons per week), and one of them was provided with the following condensing-plant:—The pan-gas and muffle-gas pass separately through about 30 ft. of 16-in pipes into an empty tower 10 to 13 ft. high and 3 ft. wide, in which a little impure acid (containing much sulphuric acid) is condensed; then into a similar tower, filled with coke, but not fed with water or weak acid (which might be done, if required, for washing and cooling the gases); then through an empty earthenware receiver into six stoneware receivers, of a capacity of 66 galls. each, and at last (after having thus passed a cooling duct of a total length of about 130 ft.) into a "plate-tower," as shown in Fig. 123. This consists of nine cylinders, 3 ft. wide and 3 ft 3 in. high, the three lowest over the bottom cylinder containing sixty Lunge-Rohrmann plates; then follows an empty cylinder, then two cylinders, filled with coke (resting on an earthenware grating), and at last two empty cylinders. The plates are supported by ring-bearers, shown in Fig. 124, 2 in. high, and tightly ground upon one another; the plates themselves have a diameter of 2 ft. 2 in. The fifteen bottom plates have holes 12 mm. wide, the next thirty-five plates holes of 7 mm., the last ten plates holes of 6 mm. The space between the outer shell and the inner cylinder, formed by the rings, is filled with pebbles. The cover of the tower is provided with an apparatus for spreading the water. The exit-pipe below leads to a "sight," serving at the same time as a regulator for the draught, and then into a flue leading to the chimney.

A first attempt to work without the six receivers was not successful, as might have been expected, the strength of the acid varying too much; also its temperature varied between 30° and 60° C. When the receivers had been set to work, the strength varied only between sp. gr. 1·161 and 1·167 at 15° C., and it averaged 1·164 at 15° C. (all specific gravities are reduced to 15° C.).

An arrangement had been made for taking samples of the acid coming down from the coke before reaching the top-plate. This acid, as a remarkable fact, showed at the pan-tower sp. gr. from 1·108 to 1·158, average 1·133, and at the muffle-tower 1·067 to 1·121, average 1·094. Of course it was impossible to imagine that a corresponding quantity of HCl could have escaped condensation on the plates, or that the 6 ft. coke could have condensed so much; evidently very much liquid acid had been carried away mechanically from the small holes in the plates by the draught, and mechanically retained by the coke. The temperature of the gases entering the first receiver in the pan-set was 15° to 55°, average 34°; in the muffle-set 15° to 59°, average 42° C.; always highest towards the end of an operation; on entering the plate-tower in the pan-set, 14° to 37° (average 24°), in the muffle-set 16° to 38° (average 28°). The acid running from the first receiver in the pan-set showed sp. gr. 1·141 to 1·170, average 1·160, in the muffle-set 1·152 to 1·175, average 1·163; between the towers and the nearest receiver in the pan-set 1·136 to 1·162, average 1·148; in the muffle-set 1·132 to 1·162, average 1·145. During October 1893, 281 charges of 8½ cwt. rock-salt each were made = 119 tons 8½ cwt., which yielded 218 tons 16½ cwt. hydrochloric acid of 1·162, or 183·2 per cent. on the rock-salt decomposed. (This is a yield not attained by *any* other condensing-plant; *cf.* Chap. IX., where the figure stated for plate-towers refers to the present case.) The temperature of the exit-gases was 30° to 40°. Mr Lasche also ascertained their acidity, but as he tested only for total acidity, without deducting SO_2 and SO_3, his figures cannot be compared with the English Alkali Inspectors' tests. Anyhow, such isolated tests, in which so much depends upon the manner of collecting the samples, etc. are not to be considered against the fact that by these plate-towers more acid was condensed, and therefore less acid must have escaped than in any other known case.

After thus proving, by a prolonged practical test, that the system, as first erected, gave absolutely satisfactory results, the owner of the works tried some further experiments. Upon removing the coke the yield fell to 169·6 per cent. acid of 1·157, which is still better than many works obtained. The best results were obtained by regulating the draught in the sights so that the anemometer in the exit-pipe showed an inward pressure of 6 mm. of water.

It was now attempted to replace the coke by adding to the sixty plates already present three plates with 5-mm. holes; but this had to be abandoned, because the draught was too much interfered with. Instead of these, eleven plates with 7-mm. holes were inserted, which caused an increase of the draught in the exit-pipe to 12 mm. water-pressure in the anemometer on the pan side, and 14 mm. on the muffle side. The yield now rose to 177·7 per cent. acid of 1·160 (1·144 to 1·161 from the pan, 1·150 to 1·164 from the muffle). Although this is decidedly a good yield, it is inferior to that obtained with the 6-ft. coke column, as was also proved by the greater acidity of the exit-gases; and it was therefore decided for the present to retain the small coke column on the top of the plates. Mr Lasche points out that probably everything needful would have been obtained without the coke, if in lieu of the fifteen plates with 12-mm. holes, plates with 7- or 6-mm holes had been employed, for the former kind of plates, the earthenware surface of which is only very small, did practically no condensing work at all, as evidenced by the fact that the tower remained quite cold up to the place where the 7-mm. holes commence. We must also add that the inner cylinder, formed by the ring-bearers, and the stationary layer of air between these and the outer shell must have greatly interfered with the radiation of heat from the tower; this has been avoided by a new design in which the ring-bearers are entirely abolished.

The Duisburg experiments have absolutely established the success of the plate-tower system for hydrochloric-acid condensation, and they have specially proved that Dr Lunge's claim that a plate-tower possesses ten to twenty times greater condensing-power than an equal space of coke-tower, is perfectly correct, although this has been impugned by Hurter.[1] Even if we comprise in our calculation the inefficient lower fifteen plates with 12-mm. holes, the inner space of the plate-tower, so far as it contains plates, is only 2 ft. 4 in. wide and 10 ft. high—that is, for both towers together just 74 cub. ft.—or, with a weekly decomposition of 30 tons salt, = 2·46 cub. ft. per ton per week. In well-conducted English works, according to the *Alkali Inspectors' Reports*, the coke-tower space for condensation averages 50 cub. ft. From this we should deduct, for the present comparison, the space occupied by the coke-column employed at Duisburg, amounting in all to 49·3 cub. ft., or 1·64 cub. ft. per ton per week, leaving 48·36 cub ft. of ordinary coke-tower space as equal in value to 2·46 cub. ft of plate-tower space. This is really about *twenty* times as much, notwithstanding that we have taken in the 12-mm. hole plates, and although the Duisburg towers suffer from the above-mentioned drawback of insufficient cooling by radiation. Nevertheless the yield of acid was better than with the most gigantic coke-towers, and the variations of strength no greater than with these.

Dr Lunge also recommends the employment of the 6-ft. coke column in addition to the plate-tower, as it costs next to nothing, and is very useful in effecting a better spreading of the water and in retaining the liquid acid mechanically carried away, and in keeping a certain stock of fresh water for washing out the last traces of HCl.

The *new design of cylinders for plate-towers*, which entirely does away with the annular bearers, is shown in Fig. 125. The cylinders are provided with four small lugs, ***a a***, for each plate. The plates are cut out in corresponding places, so that they can be let down into their proper position, whereupon they are turned a little sideways so that they rest on the lugs. The cut-out places, which would form false gas-channels, are then filled up with special wedge-shaped pieces as shown in Fig. 126.

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[1] Cf. *J. Soc. Chem. Ind.*, 1893, p. 231.

Later on[1] Lasche reports further trials with the Lunge-Rohrmann plate-towers, a little wider than those originally employed by him (*supra*, p. 327), viz., 0·803 m., but otherwise constructed in the same way, viz., with annular bearers and quartz packing between these and the outside pipes. Each tower possessed thirty plates with 7 mm. holes, and thirty with 60 mm. holes. The acid obtained averaged 20·1° Bé. (= 32·5° Tw.) at 15° C. The yield was 169·3 parts to 100 rock-salt. By removing eight plates and putting on 6 ft. of coke, the yield was increased to 183 or 184 parts of acid. Lasche ascribes the necessity of employing this layer of coke to the strong draught required, but he believes that it would be unnecessary in the case of plus-pressure furnaces.

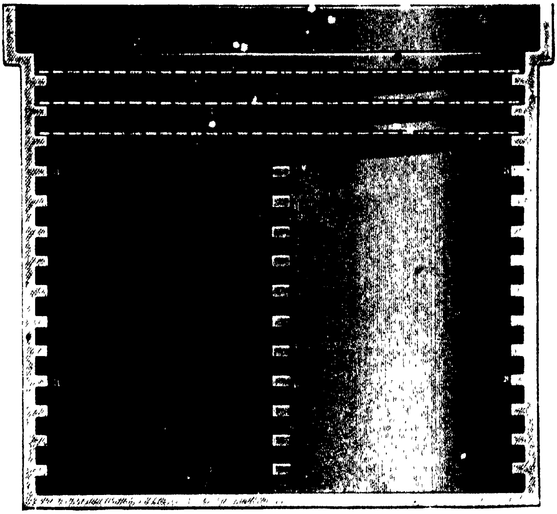

FIG. 125.

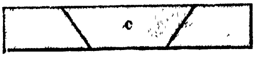

FIG. 126.

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[1] *Z. angew. Chem.* 1895, p. 374.

Niedenführ[1] confirms from his own experience the excellent results obtained elsewhere by Lasche with the Lunge-Rohrmann plate-towers in the condensation of hydrochloric acid, which in his case was rendered more than usually difficult by the employment of waste acid from the refining of petroleum for decomposing the salt, entailing a copious evolution of sulphur dioxide.

Olga Niedenführ (Ger. P. 197022) describes a few modifications of the ordinary plate-tower, such as cylinders for supporting the plates, bevelling margins of these, etc. We cannot as yet report on any practical success of these modifications. The same holds good of her Ger. P. 205963, of 1905.

Further Improvements of Hydrochloric-acid Condensers.

Special Descriptions of Packing for the Towers.—For a long time attempts have been made to replace coke as a packing material for condensers by earthenware pipes, dishes, etc. Especially since the practical success obtained by the "plate-columns" had proved that the hitherto generally accepted advantages of coke as a packing material (even later on strenuously defended by Dr Hurter) were certainly much less than assumed at that time, and were accompanied by essential drawbacks, numerous attempts have been made to attain the same result by other means. All these endeavours aim at replacing the irregular coke packing by uniformly shaped earthenware pieces, with equally uniform interstices.

For a packing to have a high absorption efficiency, it must provide:—

(*a*) A large surface of contact between gas and liquid.

(*b*) Constant relative motion at the interface of gas and liquid.

(*c*) An absence of any stagnant areas in either gas or liquid.

(*d*) An absence of any channels in the packed tower through which either gas or liquid can pass without adequate contact with the other phase.

The relative merits of the various packings depend on how well they answer the above conditions, but in addition account must be taken of the resistance to crushing and chemical disintegration, also of the cost and the tower space wasted by the bulk of the material.

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[1] *Chem. Zeit.*, 1896, p. 33.

Among the many forms of packing which have been described or patented, the following may be mentioned:—

Cups (Fig. 127), cones with a dished top (Fig. 128), pipes provided with internal partitions (Fig. 129), balls (Fig. 130), balls as patented by Guttmann, Ger. P. 91815 (Fig. 131) or by the Vereinighte Dampfziegeleien, Ger. P. 191890; plates according to Kypke, Ger. P. 97208, rhombohedra according to Scherfenberg (Fig. 132).

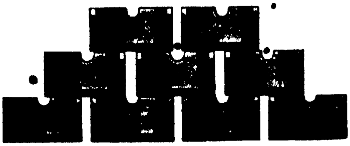

FIG. 127.

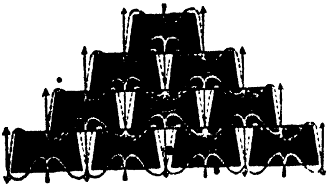

FIG. 128.

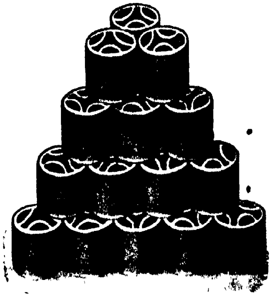

FIG. 129.

The packings shown in Figs. 130 to 133 are all bad, and only illustrate the common fallacy that a complicated design indicates thought or special knowledge. Fig. 131 is amusing, even if misleading; it would be interesting to know what causes the air-currents inside the balls. Other forms of packing are: Plates with double spirals (Plath & Hiller, Ger. P. 106718), pipes arranged in a chamber (The Baker and Adamson Chemical Company, Ger. P. 104544), porous artificial stone in the shape of cylinders or cones, open at both ends, with horizontal partitions (Wilisch, Ger. P. 173612).

The Mayor, Aldermen, and Citizens of the City of Bradford, together with Messrs Wild & Shepherd (B. P. 13001, of 1906), employ a tower, packed with layers of strips of glass, arranged

FIG. 130.

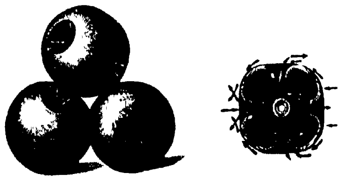

FIG. 131.

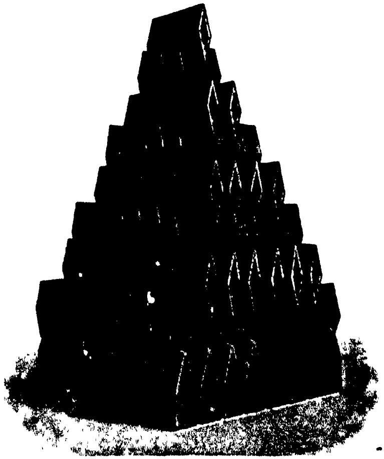

FIG. 132.

crosswise and placed on edge or in a slanting position. The ends of these strips fit into grooves of bricks, built into the casing of the tower, and are supported in this way. The height of the strips is rather less than that of the bricks, so that a space remains between each two layers.

Guttmann (B. P. 4407, of 1907) employs horizontal pieces of channel-shaped section, as shown in Fig. 133, provided with holes for the passage of the gas, and with shoulder-strips, enabling them to be built up as shown in the figure.

Petersen[1] (Fr. P. 382262) employs chambers filled with prismatic bodies having a cross-section in the shape of an Δ, the inclined faces being covered with a network of grooves packed like chequer brickwork, with either their larger or smaller parallel faces uppermost.

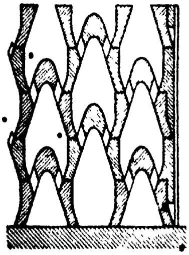

FIG. 133.

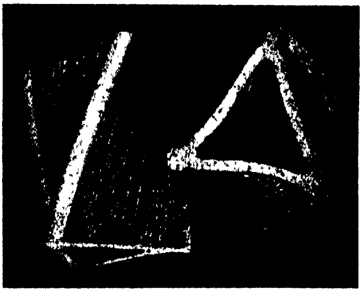

FIG. 134.

The Charlottenburger Tonwerke sell "artificial coke, made of stoneware." It has the outward appearance of gas-coke, and it is acid-resisting.

Rabe[2] discusses these proposals and describes certain "angular bodies" for packing towers.

Kussmaul (Ger. P. 194293) provides packing materials with a channel in the shape of a screw, which compels the liquid to travel over a long distance. A projection at the lowest point of the cup at the top causes the liquid to be equally distributed over the channel.

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[1] *J. Soc. Chem. Ind.*, 1907, p. 1130.

[2] *Z. angew. Chem.*, 1903, p. 437, and 1904, p. 78.

A cheap and useful form of ring packing can be obtained by using the common English field drain pipes. These are made in various diameters, the best for tower packing being 3 in. or 4 in. They are usually made 12 in. or 15 in. long, but by arrangement with the makers can be made 4 in. and 6 in long. Though much cheaper they are not as strong as rings of earthenware and should only be used on small towers, say up to 15 ft. in height.

A good shape of packing which deserves special mention is that known as "Propeller Tower Fillings" (Fig. 134). These are made by John Statham & Sons, Windsor Bridge, Manchester.

Cisterns provided with Spray-producers.

Instead of simply filling the acid-cisterns with water, and thus acting upon the gas only by a condensing-surface equal to the horizontal area of the tank, Newall and Bowman (patent of 15th June 1874) have applied a principle long known for cooling and washing gases, viz., a very finely divided spray of water. The novelty of their process only consists in the way in which the spray is produced. Fig. 135, together with the following description, will show this more clearly.

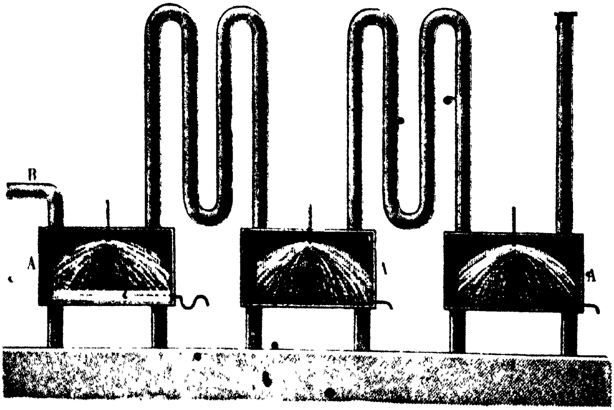

FIG. 135.

The gases are introduced into stone cisterns 6 ft. × 6 ft. and 2 ft. high: here the gas meets a spray of water filling the whole space of the trough in the shape of a fine mist, which washes the HCl out of the gas very quickly and completely, so that twelve such sprays are sufficient for four decomposing-furnaces. In this operation the latent heat of the HCl vapour becomes free, and the temperature of the gas is very much raised thereby. The gas must therefore be introduced by a number of comparatively small pipes, in order to get as much cooling-surface as possible, and the pipes must be bent upwards and downwards between each two tanks. Behind the last tank a small coke condenser should be placed about one-quarter the size of an ordinary condenser. The acid in the cisterns gets up to a strength of 33° Tw.

The principal condition is the generation of a sufficiently fine mist,[1] which is obtained by allowing the water to run, under a pressure of nearly three atmospheres, through a platinum nozzle of $\frac{1}{16}$-in. bore on to a small button of platinum fixed $\frac{1}{8}$ in. below it, from which the jet is thrown back and a very fine spray of water is generated. Since the fine outlet of the nozzle is easily stopped up, the water should be filtered. Of course, instead of water, dilute acid may be used. The inventors expected that their tanks would not interfere with the draught to the same extent as coke-towers, and that the process would therefore be applicable in many other cases—for instance, in washing copper and lead smoke, in the scrubbers of gas-works, etc. It has not, however, fulfilled the extremely high expectations with which it was at first welcomed. It has been tried in several places, but given up again. The main difficulty is that, in consequence of the very high pressure and the fine openings (both indispensable for producing a mist), the orifice of the nozzle is constantly getting stopped up, even if filtered water be used, which in itself is a very onerous condition. Recently the water-spray apparatus have been very much improved, so that more success in this line is possible.

In this connection mention may be made of Hurter's statement,[2] according to which the condensation by liquid divided into a spray is theoretically much less favourable than the other methods of condensation. Lunge showed that the basis for this calculation is a very uncertain one. Hurter contradicted this, but without adducing sufficient proof for his opinion. (For various references, see p. 242.) It is true that the condensation by spray has failed in various places, but in others it has succeeded. Thus the official *French Exhibition Report for* 1889, Class 45, p 71, states that at the Petit Quevilly works the condensation has been greatly improved by means of a water-spray in a wash-tower Many modern works use sprays in combination with their scrubbing towers and particularly in the final tower.

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[1] *Cf.* the application of this principle to Sulphuric Acid chambers, Sulphuric Acid volume.

[2] *J. Soc. Chem. Ind.* 1892, p. 227

Most spray-producers have the disadvantage that, even when the nozzle is made of platinum, the orifice is gradually

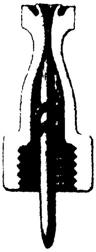

FIG. 136.

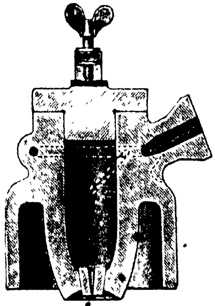

FIG. 137.

enlarged by the friction of the water forced through, so that their function is modified. Nozzles of the well-known extremely hard alloy of 90 parts platinum with 10 parts iridium would undoubtedly do better, and glass is still better. Probably Korting's spiral spray-producer, Fig. 136, has been found useful in practice.

The Deutsche Ton- und Steinzeugwerke of Charlottenburg supply tuyeres, shown in Fig. 137, made of stoneware, with an interchangeable cone, which greatly facilitates the cleaning, and which produces a mist entirely free from larger drops.

W. Feld (Ger. P. 188636) promotes the action of gases on liquids by raising the liquid by means of centrifugal force and atomising it on discs in a horizontal direction. In this manner it is projected tangentially with great velocity, whereas the gas rises round the edge of the disc and is compelled to traverse the liquid mist.

Brandenberg (B. P. 7116, of 1907) produces, by means of centrifugal force, a ring of liquid through which the gas must penetrate. If water, etc., enters a revolving cylindrical or cone-shaped vessel, centrifugal force makes it rise along the circumference, so that the bottom becomes free and the liquid assumes the shape of a floating and revolving ring. If a second (stationary) cylindrical vessel is suspended within the first, the annual space between this and the outer vessel is filled with the revolving liquid. If a gas is introduced through the bottom of the inner vessel, this penetrates into the liquid ring, rises in this and takes part in the revolution.

Very similar to this is the B. P. 23330, of 1907, of Peat and Bonin.

Korting Brothers (Ger. P. 190625) extract soluble gases and vapours or dust particles from gases by aspirating these in the well-known manner by means of an absorbing-liquid, finely divided by a spray-jet. The liquid issuing from the spray-producer is separated from the residual gas and is used over again in the purifier.

Ephraim (Ger. P 163370) removes the mist from the gases by heating these until the mist has been nearly, but not entirely gasified. In this process the bigger drops remain behind and on the subsequent cooling the vapour is condensed on their surface to form still larger drops. Ostwald (Ger. P. 195080) aims at improving this action by exposing the foggy mixture to alternate changes of pressure and temperature, preferably by means of producing suitable sounds therein. By these changes of pressure the vapour tension of the droplets is changed. On the diminution of pressure the smallest drops evaporate first; on raising the pressure the biggest drops are most enlarged, so that the changes of pressure cause an enlargement of the bigger drops at the expense of the smaller ones, and the mist is condensed.

Attention may also be directed to the "gas-filters," described on p. 404.

Special Forms of Acid-Condensers.

A *glass-tube* apparatus, constructed by Fryer, is described by the Alkali Inspectors (Fourteenth and Fifteenth Report, p. 114), and in the last edition, Vol. II., pp. 387, 388. We refer to that description, as the apparatus evidently did not answer its purpose, and was discontinued after a short time.

D. Herman (B. P. 17255, of 1887) proposed condensers consisting entirely of a large number of glass pipes, 1¼ in. wide and 3 ft. long, fitted on the top with flanges, and suspended in a frame. These pipes were to be filled with pieces of glass, and cooled outside by a current of air. From the description[1] it is clear that no such apparatus was then in existence.

Another condensing-apparatus, also consisting of glass tubes and intended for very dilute hydrochloric acid, such as is, for instance, formed in various methods for the manufacture of chlorine, has been patented by A. R. Péchiney & Co. (B. P. 6066, of 1885). It consists essentially of a stone tower, through whose sides pass a large number of glass tubes, slightly inclined against the horizontal and capable of being separately shut off. They are at their lower ends connected by india-rubber joints with a main pipe; their top ends are also fitted with india-rubber tubing, but this communicates with an open spout. Cooling-water constantly flows through the glass pipes from their lower ends, and as the outlet is above the inlet, they remain always full. The gas is conducted in the tower downwards between the glass pipes. It is very thoroughly cooled, and the acid condensed from it (further details are given in Vol. II., last edition). The gas plays round the glass pipes and the cooling-water is inside the latter, exactly opposite to Fryer's plan. This apparatus answers admirably for very dilute gases.

Hazlehurst (B. P. 1668, of 1877) describes a mechanical contrivance by which the acid gas is aspirated into the interior of a cylinder which moves upwards and downwards in another vessel, filled with water and dilute acid, in the manner of a piston. On the descent of this hollow piston it forces the previously separated gas through the liquid contained in the outer cylinder and forming a hydraulic lute.

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[1] *J. Soc. Chem. Ind.*, 1890, p. 147.

Hannay (B. P. 16290, of 1886) describes a condensing-apparatus on the following principle:—Perpendicular nets are suspended in a trough through which water is constantly flowing and into which the bottoms of the nets dip.

Weidig and Remmey (B. P. 1082, of 1888) construct absorbing-towers of a number of superposed earthenware cylinders (Fig. 138), closed at the bottom, open at the top, with an inner overflow, E, about four-fifths way up, on alternate sides, through which each cylinder communicates with that next below. Each cylinder also has an outer projection, F, open at the top, at the same height as the overflows E. Two such towers are combined The gas descends in one and ascends in the other, and on its way gives up its HCl to the water standing in the cylinders. When the acid has got up to strength in one of the towers, the gaseous current is reversed, so as to descend in the second and to ascend in the first tower. When the acid in both towers is up to strength, the troughs are emptied by siphons through the open projections F, and are recharged with water. [This apparatus might replace the ordinary stoneware Woulfe's bottles, where economy of space is an object, but it will probably act not much better than these.]

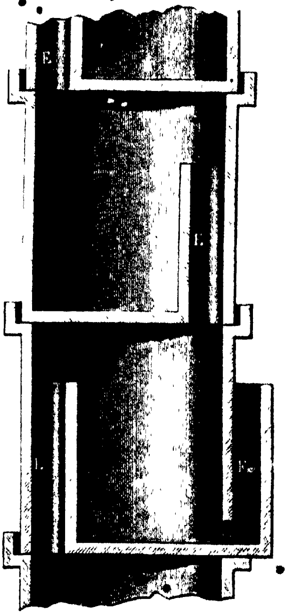

Fig. 138.

Doulton and Sauceau (B. Ps. 14766 and 14768, of 1894) describe a tower built up of stoneware cylinders, packed with short cylinders perforated alternately in the centre and at the sides, or tiles perforated in various ways.

The Baker and Adamson Chemical Co. (Ger. P. 104544) employ a number of cylinders, arranged for catching the liquid at alternate ends; at one side they communicate with a common gas-dividing chamber, at the opposite side with a chamber from which the residual gases can escape outside.

Barbier (B. P. 14014, of 1905) employs an outside tower and an inner concentric cooling-pipe. The space between these is fitted with a number of cups. *Cf.* also his B. P. 7565, of 1898, and Hart's U.S. P. 601466.

Rabe has constructed "cooling-elements" (supplied by the Deutsche Ton- und Steinzeugwerke, of Charlottenburg), which may be applied to any kind of condensers (also to plate-columns); they are provided with separate water-pipes, and thus prevent any injurious rise of temperature.

Olga Niedenfuhr (Ger. P. 195525) also provides the condensing-towers with cooling-pipes, one end of which passes through the side of the tower, all of them being connected with an outside water-conduit. A modification of this consists of single pipe-elements, combined to long strings by means of connecting-arches and placed in cooling-boxes.

Internal cooling by pipes in which water is circulated is also proposed by E. Leblanc (Fr. P. 462712, of 1913).

The Westdeutsche Steinzeugwerke and the Euskirchen factory employ condensers with undulated sides.[1]

Kubierschky (Ger. P. 194567, of 1908) constructs apparatus for the special cases of gases which get *heavier* by their action with absorbing liquids (*e.g.*, when expelling bromine by steam), which does not apply to our case.

Employment of Special Absorbents for Hydrochloric Acid.

A proposal made by Precht (Ger. P. 19769) was intended not merely for removing HCl from furnace-gases, but also for utilising it. The HCl was to be absorbed by spent bone-charcoal from sugar-works, the calcined carbonate thus decomposed and the "char" revivified. This proposal is of course only applicable under quite exceptional circumstances; and it suffers under the drawback that the SO_2 and SO_3 of the furnace-gases must have a very injurious action on the char.

Another process for removing HCl gas from its mixture with air has been patented by Buisine (Fr. P. 222801). He employs pyrites-cinders, moistened with water, which are said to very completely absorb the hydrochloric acid. According to the circumstances, either solid ferric chloride or a solution of the same is formed and is utilised at will.

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[1] *Chem. Zeit.*, 1907, pp. 9, 202.

At the Uetikon chemical works near Zurich the last traces of HCl from saltcake-furnace gases are removed by passing them through finely divided metallic tin, and collecting the stannous chloride formed.

Carulla (B. P. 19920, of 1909) proposes the use of iron for the same purpose. Some or all of the receivers or towers are packed with scrap-iron or mild steel, ferrous chloride being thus formed and hydrogen evolved. The chloride is then converted, by precipitation, into iron oxide (*e.g.*, as in B. P. 27302, of 1908; *J. Chem. Soc.*, 1909, 1126), and, since very dilute solutions are preferable for this purpose, the absorption of the last traces of hydrochloric acid is rendered very easy by this process, the ferrous liquor plant being conveniently placed at the end of the system, and hydrochloric acid of high strength being produced, if desired, in intermediate parts of the plant.

CHAPTER IX

MANUFACTURE OF HYDROCHLORIC ACID BY OTHER THAN THE ORDINARY METHODS

A. *From Sodium Chloride.*

IT is a very natural question whether it would not be possible to decompose sodium chloride, without employing sulphuric acid, in such manner that, besides hydrochloric acid, a substance of greater value than sodium sulphate is produced. Many attempts have been made at decomposing sodium chloride by superheated steam, by silica, alumina, and many other substances, or by electrolysis; some of these proposals are better treated when speaking of the manufacture of alkali, and others in that of chlorine. Here we shall merely mention proposals in which the hydrochloric acid is the principal product considered.

Heating *sodium chloride, mixed with clay, in a current of steam*, according to Vorster and Grüneberg, produces sodium silicate and HCl. But the temperature required is so high, and the wear and tear of the apparatus so great, that this process is not practicable. Gorgeu[1] has studied the conditions of this reaction and finds that clay, with 35 per cent. Al_2O_3, is able to decompose 22 per cent. of its weight of NaCl in a current of steam at a dark red heat.

It is interesting to note that Sidgewicke obtained a British patent (No. 641) in 1749 for the manufacture of hydrochloric acid from salt and clay (*cf.* p. 73).

The *Kayser Patent Company* (Ger. P. 63223) mixes clay with rock-salt, and moulds this into blocks, dries and heats by gaseous fuel in furnaces of peculiar construction. The hydrochloric acid is condensed, and the fused sodio-aluminium silicate running off at the bottom is worked for soda.

[1] *Comptes rend.*, 102, 1164.

Klein (Fr. P. 368106, of 1906) proposes that bauxite, clay, or other aluminous bodies, in fine powder, be added to sodium chloride melted in a closed vessel, connected with apparatus for condensing the hydrochloric acid evolved. Superheated steam is injected into the melt during the process. The mass is lixiviated, and carbon dioxide is passed into the cleared solution of sodium aluminate obtained. The aluminium hydroxide precipitated is removed, and the filtrate evaporated to recover sodium carbonate. The process may be repeated with the aluminium hydroxide thus obtained, in which case the injection of steam, except towards the end of the process, may be dispensed with.

A series of patents have been taken out for the manufacture of hydrochloric acid and silico-aluminates by the Electric Smelting and Aluminium Co of Lockport, N.Y. (U.S. Ps. 1040977; 1040893; 1040894; 1040895; 1040977; 1041598; and 1041599, all of 1912). The detail given suggests that the process was being put into operation, but the main purpose is probably the preparation of alumina for the manufacture of aluminium.

For a patent with a similar object, but using chlorine to disintegrate the clay, see Patronilleau, Fr. P. 481106, of 1916.

From *manganous chloride, common salt, and sulphur dioxide*, and air, Daguin and Co. propose to make hydrochloric acid (B. P. 3669, of 1888). Air, mixed with 10 per cent. SO_2, is to be passed into a boiling solution containing 250 kg. NaCl and 270 $MnCl_2$ per cubic metre. The following reactions are believed to take place, in which the manganese salt acts as a catalytic agent:—

1. $2NaCl + MnCl_2 + SO_2 + O + H_2O = MnSO_4 + 2NaCl + 2HCl.$
2. $MnSO_4 + 2NaCl + 2HCl = Na_2SO_4 + MnCl_2.$

The chlorides of calcium or magnesium can be treated in the same way. The HCl is distilled off, or is converted into chlorine by manganese dioxide. As the inventors do not even say how the sodium sulphate is to be separated from the manganous chloride, we need not detain ourselves with this proposal.

Th. Meyer (Ger. P. 186398) prepares dry HCl from common salt and sulphuric acid, obtaining at the same time sodium *bisulphate*, which is prevented from solidifying. He finds that sodium chloride dissolves completely in a sufficient excess of liquid bisulphate, that sulphuric acid of at least 80 per cent. H_2SO_4 may be added to hot bisulphate without any frothing, and that such acid may be made to circulate in the bisulphate. Hence he decomposes NaCl in a medium of liquefied, hot bisulphate, introducing in an appropriate place, either continuously or from time to time, a stream of sulphuric acid of at least 90 per cent. H_2SO_4, employing a quantity corresponding to that of the NaCl introduced, whilst on the opposite side a corresponding quantity of bisulphate is run off. This process is intended to be carried out in connection with that described in Ger. P. 136998, and mentioned *supra*, pp. 183 *et seq.*, for utilising nitre-cake, but it is not known if it is in operation.

The General Chemical Co. (B. P. 9875, of 1902; U.S. P. 698704) prepare HCl by heating 2NaCl with $1Na_2S_2O_7$ (sodium pyrosulphate) in retorts, into which steam is passed.

Trivick (U.S. P. 728335) heats 2NaCl with $4H_2SO_4$, and thereby obtains gaseous HCl and fused *tetrasulphate*, $Na_2O(SO_3)_4$, which after cooling is granulated, and on being dissolved in water may be used in lieu of strong sulphuric acid.

Hipp (U.S. P. 726533) heats nitre-cake, purified to some extent, with common salt, and thereby liberates HCl.

B. *From Calcium Chloride.*

Calcium chloride is obtained as a waste product of various chemical industries in enormous quantities, and it has very few direct applications. It can be obtained in any desired quantity from the Weldon chlorine process, and even more extensively from the ammonia-soda process.

It seems that Pelouze[1] was the first to point out that calcium chloride, mixed with sand in order to prevent fusion, is almost completely decomposed by steam at a red heat, with copious evolution of HCl. This process was taken up by Solvay for utilising the calcium chloride from the ammonia-soda manufacture (B. Ps. 27, 91, and 171, of 1877). The solution of calcium (or magnesium) chloride is brought to dryness; the residue is moulded into balls, etc., with sand or clay; these are put in iron or brick towers, heated from the outside, and a current of superheated steam is passed through. Hydro[illegible] chloride is evolved and is condensed in the usual manner, or allowed to act upon the silicates and aluminates of lime or magnesia produced, thus obtaining on the one hand recovered $CaCl_2$ or $MgCl_2$, on the other hand finely precipitated silica or alumina. The silicates and aluminates can be used directly for decomposing a solution of ammonium chloride. At a very high temperature alumina acts as an acid and expels HCl from $CaCl_2$ or $MgCl_2$. This is also the case with aluminium silicate and o[illegible] course with silica itself, so that the silicates and aluminates of calcium and magnesium are formed. With calcium chloride at least an equal quantity of the earthy substances must be tak[illegible]; $MgCl_2$ requires rather less. The practical success of this process was not satisfactory.

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[1] *Comptes rend.*, 88, 1267.

In Solvay's Ger. P. 13528, a furnace, intended for the above purpose, is described, in which the air (for the manufacture of chlorine) or the steam (for that of HCl) is first passed through residue already treated, and there receives a first heating. In his B.P. 7260, of 1885, the most suitable quantities of silica and alumina are discussed. It is proposed to add to the mixture a certain quantity of the residue from a former operation, in order to obtain an infusible residue, suitable for cement.

Kayser, Williams, and Young (B. Ps. 11492 and 11494, of 1887) describe exactly the same process, with a special furnace. W. Walker, again, patents the decomposition of calcium chloride (mixed with salt) by sand; the residue to be used for glass-making (B. P. 2019, of 1891).

Lunge made some experiments on this reaction, with the following results[1]:—On igniting calcium chloride with its equivalent of silica (kieselguhr) in a current of steam, from 60·5 to 66·8 per cent. of the theoretical quantity of HCl was obtained; on igniting 2 parts of felspar with 1 part $CaCl_2$, 66 per cent. of the chloride was obtained as HCl, and no alumina soluble in acid was found in the residue. But even on heating $CaCl_2$ by itself in a current of steam at a moderate red heat, 54 per cent., at a bright red heat 60 per cent. of the possible HCl was obtained, the residue showing a strongly alkaline reaction. Hence the addition of silica or felspar did not produce any favourable result.

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[1] *Dingl. polyt. J.*, **248**, 360; *Fischer's Jahresber.*, 1882, p. 374.

The hydrochloric-acid vapour obtained by Solvay's methods is at the best greatly diluted, which led to his proposals, mentioned on p. 394, for obtaining strong HCl by means of calcium chloride solutions; but these are neither simple nor cheap.

Hurter[1] points out that with a 20 per cent. solution of calcium chloride and HCl gas, diluted by steam to 5 per cent., 1000 tons of water must be evaporated for each 100 tons of $CaCl_2$, as it is obtained from the ammonia-soda manufacture, in order to bring the solution to its original concentration. If we consider that the decomposition of $CaCl_2$ by steam is an endothermic reaction, absorbing 26,000 calories per gram-molecule of HCl, and that the reaction therefore requires much time, labour, and apparatus, this method of producing hydrochloric acid does not stand much chance of economic success.

Twynam (B. P. 731, of 1885) proposes treating calcium chloride liquors at 80° C. with lime, in order to precipitate calcium oxychloride, from which chlorine is to be made with dry air, or hydrochloric acid with air and steam. [This would probably be even more difficult than with pure $CaCl_2$.]

Bramley (B. P. 8289, of 1887) mixes $CaCl_2$ with calcined iron-ore and heats in a current of air to produce chlorine, or in steam to produce HCl; the residue is to be worked for iron.

Jung and Steuer (Ger. P. 91205) add to calcium chloride solutions (especially such as result in the ammonia-soda process), after suitable concentration, a solution of cupric sulphate, besides a precipitate of calcium sulphate. Into the solution of cupric chloride thus formed they pass hydrogen sulphide, obtained by reducing the calcium sulphate, formed in the first operation, to sulphide by igniting it with coal, and working the CaS for H_2S by the Chance-Claus process. The cupric sulphide is retransformed into sulphate by oxidation. This process is so complicated that it appears unlikely it would prove remunerative, and the same criticism applies to the process of Schwarz and Weishut (Ger. P. 96158). They evaporate the calcium chloride liquors to dryness, fuse the residue with barium sulphate and coal, extract the barium chloride thus formed, precipitate the solution with sodium sulphate, evaporate the solution of sodium chloride thus formed, and transform the dry NaCl into sulphate recovering the HCl in this process.

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[1] *J. Soc. Chem. Ind.*, 1883, p. 103.

Schollmeyer (Ger. P. 191890) gently heats calcium chloride with hydrofluosilicic acid, till all HCl is expelled:

$$CaCl_2 + H_2SiF_6 = CaSiF_6 + 2HCl.$$

The residual solution is evaporated to dryness and heated till all silicon fluoride has been expelled:

$$CaSiF_6 = CaF_2 + SiF_4.$$

This gas is brought into contact with water, thus regenerating two-thirds of the acid originally employed:

$$3SiF_4 + 2H_2O = SiO_2 + 2H_2SiF_6.$$

This process furnishes highly concentrated hydrochloric acid, free from arsenic and sulphuric acid, together with pure calcium fluoride and silicic acid.

From fused calcium chloride Seamon (U.S. P. 826614) prepares HCl by passing acetylene through it, obtaining calcium carbide as by-product.

The attempts to prepare hydrochloric acid from calcium chloride have been made principally in order to utilise the waste liquor of the ammonia-soda manufacture. But experience has shown that the production of hydrochloric acid (or chlorine) from calcium chloride succeeds only partially and only by employing such an amount of heat that the hydrochloric acid thus obtained costs more than that made by the ordinary process. So long as that acid has its present low value, all endeavours for utilising waste liquor appear to be hopeless.

C. *From Magnesium Chloride.*

Hydrated magnesium chloride is much more readily hydrolysed than calcium chloride. Davy and Graham mention the decomposition of magnesium chloride on heating. Even in evaporating a solution of $MgCl_2$, evolution of HCl occurs as soon as there is less than 6 mols H_2O present to 1 mol. $MgCl_2$. On further heating, so much HCl escapes that it was formerly believed to lead to a complete realisation of the reaction $MgCl_2 + H_2O = MgO + 2HCl$. Many proposals for preparing HCl or chlorine are founded on this assumption. The proposals for the preparation of chlorine are dealt with in another volume, and in this volume reference is made only to proposals for making hydrochloric acid. Magnesium chloride is certainly far from being such a frequent waste product of other chemical manufactures as calcium chloride, but in the manufacture of potassium salts at Stassfurt alone, sufficient $MgCl_2$ is formed to cover all the present needs of the whole world as regards hydrochloric acid and chlorine. In the working up of the mother-liquors of sea-water, large quantities of $MgCl_2$ are also formed, none of which has yet been utilised. The hydrolysis of magnesium chloride has frequently been noted by inventors, who proposed to replace lime by magnesia in the manufacture of ammonia soda, in order to liberate the HCl from the $MgCl_2$ formed. It may be said at once that these attempts have not been successful. Most proposals for utilising magnesium chloride have only been tried experimentally, if at all. A few of them have been worked out with the expenditure of much energy and capital, but mostly for the direct manufacture of chlorine. It seems that at Stassfurt some hydrochloric acid is made from magnesium chloride, but it is not known under what circumstances and with what economic success.

Eschellmann has published a very elaborate paper on the methods for producing chlorine and hydrochloric acid from magnesium chloride.[1] According to him the production of $MgCl_2$ at Stassfurt, in the form of saturated "final liquor," at that time was about 200,000 tons per annum, equal to 150,000 tons of chlorine, which would be more than sufficient to furnish all the bleaching-powder, chlorate of potash, and hydrochloric acid consumed at that period in the whole world. This is, however, based on the assumption that the Weldon-Péchiney process would be generally introduced, but this has not been the case. A similar estimate is made by Kosmann in his pamphlet, *Die Darstellung von Chlor und Chlorwasserstoffsaure aus Chlormagnesium* (Berlin, 1891); he even states 200,000 tons as the quantity of $MgCl_2$ *lost*, exclusive of that which was actually used.

Eschellmann describes a number of carefully executed laboratory experiments, which show that, on heating $MgCl_2,6H_2O$ to 250° just one third of the Cl is split off as HCl the residue being $2MgO,4MgCl_2,3H_2O$. On further heating up to 350° no change occurs; but from this point there is a fresh evolution of HCl, and at 550° this reaction proceeds so far that one-half of the HCl is expelled, and the compound $MgO,MgCl_2$ remains as a white, crystalline, brittle, silky mass, which is decomposed by water, with evolution of much heat. It makes no difference whether $MgCl_2,6H_2O$ is heated by itself or in a current of nitrogen.

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[1] *Chem. Ind.*, 1889, pp. 2, 25, 51.

Eschellmann gives the following thermochemical data for the conversion of magnesium chloride into MgO and HCl or chlorine:—

	K.
I. *For Hydrochloric Acid:*—	
Decomposition of $MgCl_2$	−151
" $MgCl_2, 6H_2O$	− 33
" H_2O	− 58
Evaporation of $5H_2O$	− 59
	−301
Formation of MgO + 147 " 2HCl + 44	+191
Heat absorbed in the process	−110
II. *For Chlorine:*—	K.
Decomposition of $MgCl_2$	−151
" $MgCl_2, 6H_2O$	− 33
Evaporation of $6H_2O$	− 70·6
	−254·6
Formation of MgO	+147
Heat absorbed in the process	−107·6

F. Fischer[1] gives similar calculations, applied to the Péchiney-Weldon chlorine process, which employs magnesium oxychloride.

In both cases, even under the theoretically best conditions, a very large amount of heat is required for carrying out the reaction; it is evident therefore that all processes for manufacturing HCl and chlorine from magnesium chloride must be burdened with a very large consumption of fuel. An inference, not stated by Eschellmann, but deducible from the above data, is that it is in all circumstances less profitable to produce hydrochloric acid from magnesium chloride, than to produce chlorine, more heat being consumed in the former than in the latter case. But at present there is no process for making chlorine from magnesium chloride in which there is not also a copious and sometimes even excessive production of hydrochloric acid as a by-product. Lunge,[1] in a criticism of the above, offers a warning against relying on the application of thermochemical data.

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[1] *Z. angew. Chem.*, 1888, p. 549.

In the following pages Eschellmann's convenient classification of the various proposals for making HCl from $MgCl_2$ has been adopted.

1. *Heating* $MgCl_2,6H_2O$ *and Steam externally.*—As early as 1864 Clemm[2] described the manufacture of hydrochloric acid by heating magnesium chloride in a saltcake muffle-furnace with superheated steam. Weldon, in 1869, took out a British patent for the same invention, which he abandoned on learning of Clemm's process. M'Dougall (B. P. 2048, of 1886) applied the same process to magnesium chloride obtained in the ammonia-soda process by decomposing NH_4Cl with MgO. Wilson (B. P. 3098, of 1885) patents practically the same thing as Weldon (*cf.* below).

Heinzerling and Schmid (B. P. 13648, of 1888) prescribe decomposing the magnesium chloride in a shelf-furnace with hollow, heated plates, exactly similar to a blende-roasting furnace. The material, previously partially decomposed in a muffle-furnace or the like, is introduced by feeding-rollers at the top and is gradually moved downwards to the lowest, hottest shelf, from which it is discharged. They describe improvements of this process in Ger. P. 48845. Eschellmann points out that the principle of counter-currents had already been similarly applied by Weldon in 1881; but the application of the heated shelves was a novelty.

The advantage claimed by this class of processes consists in not having to dilute the gases containing the HCl, and the consequent purity and easier condensation of the acid. But this is, according to Eschellmann, counterbalanced by greater drawbacks, especially the difficulty of supplying the heat from without, which is all the greater as the apparatus cannot be made of iron, and must be made of stone. The steam must also be superheated and does not act perfectly, because it does not pass through the mass, but merely over it. Lunge suggests that both of these drawbacks could be avoided. Instead of heating the mass from without, Péchiney's apparatus might be employed. This has narrow slits in the brickwork, alternately heated from within, and afterwards giving up that heat to the substance to be decomposed. The action of steam might be promoted by mechanical means, though this has the disadvantage of bringing hot acid-gases in contact with iron.

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[1] *Z. angew. Chem.*, 1888, p. 95. [2] *Z. Verein deutsch. Ingen.*, 8.

2. *Mixing magnesium chloride with salts which lose their water only at high temperatures, heating the mixture, and recovery of the salts.*—For this group of methods Eschellmann claims the priority, but he overlooked a British patent taken out eighteen years before his (C. G. Clemm, 1776, of 1863), though Clemm did not commence with magnesium chloride obtained as a refuse salt, but with kieserite, which subsequently leads to the formation of $MgCl_2$. Clemm dissolves 1 mol. $MgSO_4$ and 1 mol NaCl in as little water as possible, mixes the solutions, evaporates to dryness, and heats the residue in a current of steam in a muffle-furnace. In this process the double salt $MgSO_4,Na_2SO_4$ is formed, together with a little MgO and HCl. From the muffle-furnace the mass is conveyed into a reverberatory furnace, in which the HCl is said to be almost entirely expelled. The residue, containing the abovementioned double salt, is dissolved in water; from this solution one can either obtain anhydrous sodium sulphate by boiling and fishing out, or crystallised Glauber's salt by freezing. There is also the possibility of first making Glauber's salt by freezing from a solution of $2NaCl+1MgSO_4$ (*cf.* p. 192), and then working the $MgCl_2$ remaining in the mother-liquor for HCl by evaporating and heating in a current of steam.

Eschellmann himself (Ger. P. 17058) proposed mixing kieserite or Epsom salts with the magnesium salt (the patent also mentions calcium sulphate, or calcium chloride + magnesium sulphate), igniting and separating the magnesium sulphate from the magnesia formed by dissolving in water, in order to reproduce Epsom salts. He also says that the practical utilisation of the process was frustrated by the cost of heating the mixture and recovering the sulphate—reasons which of course are valid for all other proposals of the same class.

Konther (Ger. P. 41351) mixes magnesium chloride with at least its equivalent of calcium chloride and water and heats to fusion. The calcium chloride retains the water so long that it escapes at last as superheated steam, and decomposes the magnesium oxychloride. The residue is separated by water into magnesia and solution of calcium chloride, and the latter is again used after evaporation.

P. de Wilde (Ger. P. 59155) begins like Eschellmann and Konther, but instead of lixiviating the residue by water in order to separate the magnesia, he grinds it into powder, introduces this into concentrated $MgCl_2$ liquor (*e.g.* "final liquor" from the potassium chloride manufacture), evaporates the mixture to the consistency of a paste, and ignites in a black-ash furnace. The residue, which is now richer in magnesia, is used a second or third time for decomposing $MgCl_2$ liquors. The last residue, now very rich in magnesia, is lixiviated with hot water, which leaves magnesium hydroxide behind, whilst $MgSO_4$ or $CaCl_2$ enter into solution. He asserts that he obtains 96 per cent. of the total chlorine in the shape of HCl.

Bohlig and Heyne (Ger. P. 39566) propose decomposing $MgCl_2$ completely into MgO and HCl by mixing its solution with coarse sawdust, and gradually heating the damp mixture in retorts to a dark red heat, till the evolution of gas has ceased. The concentration of the liquor must be chosen in such manner that the magnesia-charcoal thus formed does not contain much above 40 per cent MgO; otherwise, even on strongly heating, the decomposition is only partial. The magnesia-charcoal is to be employed for the purification of water, according to a well-known process of the same inventors. Eschellmann classes this process with the same group as the last, because from the sawdust, by heating without contact with air, steam is formed which acts upon the magnesium oxychloride and decomposes it. Of course the hydrochloric acid produced by this process must be very impure, and the drawback of heating externally exists in this case also.

2. *Heating* $MgCl_2,6H_2O$ *by direct flame with supply of steam, with or without addition of other substances.*—To this class belong the numerous Solvay patents, taken out since 1877, and intended in the first instance for calcium chloride. As a matter of fact, practical trials seem to have been made only with $CaCl_2$, and these in recent years mostly with the intention of producing not HCl but chlorine, by employing air in place of steam. As

regards magnesium chloride, all proposals for mixing with it sand, clay, or similar foreign substances are useless, since the magnesia cannot be recovered from them (this admixture was first patented in 1870 by H. M. Baker).

Ramdohr Brothers (Ger. Ps. 11540 and 11746) propose evaporating magnesium chloride solution, and igniting the residue with an oxidising flame and superheated steam. The escaping HCl is condensed; the residue, consisting of $MgCl_2$ and MgO, is moulded into bricks with clay and iron-ore, and is burnt (in this instance the manufacture of these bricks was the principal object). Ramdohr, Blumenthal, & Co. (Ger. P. 19259) evaporate the $MgCl_2$ solution to sp. gr. 1·4 or 1·5, so as to leave essentially $MgCl_2,6H_2O$, then add from 4 to 10 per cent. magnesite, and heat the mixture in a current of air to red heat till the evolution of HCl [and chlorine!] ceases. The remaining magnesium oxychloride is decomposed into MgO and $MgCl_2$ by heating with water. Ramdohr[1] elsewhere asserts that magnesium chloride can be *completely* decomposed by an oxidising flame and highly superheated steam, furnishing pure MgO and hydrochloric acid of 34° Tw. The magnesia can be utilised in various ways, principally by calcining at the highest white heat, when it yields very hard and extremely fireproof bricks.

Vogt (Ger. P. 37083) describes an apparatus for decomposing $MgCl_2$ liquors, consisting of a revolving furnace in which the liquid $MgCl_2$ is evaporated to dryness by producer-gas; this flame comes from a shelf-furnace in which the dry magnesium chloride, being moved from shelf to shelf, is gradually decomposed into MgO and HCl.

Almost at the same time as Ramdohr, Blumenthal, & Co. took out their German patent in 1881, Weldon obtained a British patent, almost precisely agreeing with it, for making from concentrated magnesium chloride solution and magnesia a solid oxychloride, which is crushed into pieces and, in a set of eight iron cylinders arranged in regular rotation, treated either with steam (for HCl) or with air (for chlorine). This proposal was frustrated by the impossibility of using an iron apparatus, but it gave occasion for working out the Weldon-Péchiney chlorine process. According to theory as well as the patent specifications, the Weldon process, as modified by Péchiney, would be applicable to the manufacture of hydrochloric acid, but this has never been attempted in practice.

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[1] *Fischer's Jahresber.*, 1482, p. 421.

Friedrich (Fr. P. 449733, of 1912) describes a process of heating magnesium chloride, with or without calcium chloride, in such manner that the material is brought into intimate contact with the burning fuel (solid, liquid, or gaseous), and water or steam is injected when necessary. The air supplied is advantageously heated, and may be mixed with furnace gases at a high temperature.

Schwarzenauer (Ger. P. 279008, of 1914) uses a vertical retort and introduces superheated steam at the bottom, the hydrochloric acid being led off at the top. Schloesing (below) recommends passing the gases in the reverse direction.

J. Wilson (B. P. 3098, of 1885) evaporates $MgCl_2$ liquor up to the point where it would solidify on cooling, and then runs it into the decomposing furnace, which still contains residues from a former operation, by which the liquor is absorbed. The mixture is heated with air to obtain chlorine, or with steam to obtain HCl. [This process does not essentially differ from that of Weldon's, just mentioned.]

Nithack (Ger. P. 30742) brings hot, very concentrated solutions of magnesium chloride, in the state of spray, into contact with fire-gases, hot brickwork, etc. Kosmann[1] unfavourably criticises this proposal.

A number of German patents have been taken out by the Salzbergwerk Neustassfurt (Nos. 36673, 46215, 47043, 48552, 51209, 54830). They employ reverberatory furnaces, with several floors placed one above the other, sometimes connected with kilns, in various combinations. The later patents exchange the open furnaces for muffles, the kilns for retorts, and revert to the Solvay type of apparatus. There are, *e.g.*, retorts made of firebricks, with fire-flues at both sides, 6 in. wide, 5 ft. long, and 10 ft. high, with working holes at the narrow ends. They are heated from without by fire-gases, which travel first in a flue below, then upwards, divided into a number of vertical flues, then again downwards by lateral flues.

The Vereinigten chemischen Fabriken at Leopoldshall (Ger. P. 43500) describe a mechanical apparatus for moulding magnesium oxychloride, evidently intended for producing HCl or Cl according to the principle described above.

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[1] *Loc. cit.*, p. 955.

Schloesing (Fr. P. 360356, of 1905) precipitates as gypsum the sulphates present in commercial magnesium chloride, by means of calcium chloride, evaporates the solution at a temperature of 160° C., precipitates the excess of calcium chloride as calcium sulphate by means of magnesium sulphate, cools down, separates the liquid from the precipitated salts, and heats it with MgO, so that $MgO,MgCl_2$ is formed, which, on heating in a furnace, splits off HCl.

In a later patent (Fr. P. 394037, of 1908) Schloesing modifies this process as follows:—To the solution of magnesium chloride, heated to 132° to 133° C., powdered magnesia is added to the extent of one-third that required to form the ordinary oxychloride ($MgCl_2,MgO,6H_2O$). Heating and stirring are continued, until the mixture becomes pasty, when it is turned out and moulded into briquettes. These are dried at a low temperature (200° C.), and are then decomposed at a dull red heat, the decomposition into magnesium oxide and hydrochloric acid being effected by spreading the material on interspaced bars of refractory material in a heating chamber, and passing the hot gases from an adjacent furnace or producer through the mass, from above downwards, in order to avoid crushing the friable product, steam being introduced into the chamber as required.

4. *Other Proposed Methods.*—Rosenthal (Ger. P. 31357) proposes obtaining hydrochloric acid by evaporating sulphate of alumina with magnesium chloride solution, the reaction being:

$$Al_2(SO_4)_3 + 3MgCl_2 + 3H_2O = Al_2O_3 + 3MgSO_4 + 6HCl.$$

The *alumina* would be the principal product in this case. In order to separate the last 4 to 7 per cent. of the sulphuric acid, which cannot be removed from the alumina by heat alone, a little lime is to be added to the mixture, and steam superheated to 300° is to be passed through in closed vessels. The alumina is further to be purified from iron by a special process, described in the patent.

Lyte and Tatters (B. P. 17218, of 1889) propose making hydrochloric acid by treating anhydrous magnesium chloride or magnesium oxychloride with sulphuretted hydrogen (formed from alkali waste and carbonic acid) and just sufficient air, at a temperature between 300° to 430°. Under these conditions it is claimed that no sulphur dioxide (which would give hydrochloric acid and sulphur) is formed. This proposal does not appear very practical.

Dieffenbach and Moldenhauer (Ger. P. 203080, of 1906) obtained a nearly perfect decomposition of magnesium chloride into MgO and HCl without introducing steam, thereby obtaining nearly anhydrous hydrogen chloride gas. When heating MgO, HCl, no further decomposition takes place between 350° to 500° C., if the gaseous mixture of HCl and steam is allowed to remain over the oxychloride so that the equilibrium is not disturbed. On further heating, the decomposition sets in slowly; more strongly only from 750° onwards. If, therefore, the temperature is raised quickly and without essential disturbance of the equilibrium beyond 750°, hardly anything escapes afterwards but dry HCl. The inventors describe a muffle suitable for this purpose, and give further instructions for working the process.

M. Sandecker and L. Weiss (Ger. P. 223169, of 1908) propose to prepare hydrochloric acid from liquors containing calcium chloride or magnesium chloride in an unusual manner. The liquors are treated with boric acid or an acid phosphate of an alkaline-earth metal or of magnesium, and the solution is forced through a jet into a heated vessel. By addition of an oxidising agent, chlorine is obtained instead of hydrochloric acid. The residual liquor, if boric acid has been used, is heated with ammonium chloride, whereby ammonia is liberated and a mixture of boric acid and calcium or magnesium chloride is left, ready for the production of a further quantity of hydrochloric acid or chlorine. When an acid phosphate is used, this may be regenerated from the residual liquor by treatment with sulphur dioxide or carbon dioxide.

Kerr (U.S. P. 1203357, of 1916) makes hydrochloric acid by heating together to about 200° a mixture of nitre cake and magnesium chloride.

General Remarks on the Manufacture of HCl *from Magnesium Chloride.*

Eschellmann gives[1] a calculation for hydrochloric acid made from magnesium chloride, founded entirely on theoretical assumptions. For 1000 kg. acid of 32° Tw., = 320 kg. HCl, we require 417 kg. $MgCl_2$ = 1484 kg. "final liquor" of the potassium chloride manufacture, which has no commercial value, but must be evaporated from sp. gr. 1·16 to sp. gr. 1·45. He calculates as follows (figures for 1889):—

	Mark.
Evaporating the final liquor	8·00
Coal for decomposing it (four times the theoretical quantity), 259 kg.	2·57
Superheating the steam	0·33
Condensation	1·00
Labour, water, interest on capital	3·10
Cost of 1000 kg. acid of 32° Tw.	15·00

There is no allowance for wear and tear and repairs, which must be very heavy in this case. Moreover, such estimates are usually below the truth. On the other hand, the value of the magnesia must be allowed for as well.

In 1907 three factories in the Stassfurt district together made 12,000 tons hydrochloric acid per annum from magnesium chloride[2]

The reason why up to this date most of the magnesium chloride liquors, resulting from the manufacture of potassium chloride, are run to waste is that the electrolytic chlorine processes, as well as the large demand for saltcake by the glass industry and the consequent production of HCl, have made a further extension of special processes for the manufacture of hydrochloric acid unremunerative in most cases. At the present time over 70 per cent. of the German demand for chlorine is supplied by electrolysis, so that several manufacturers of Weldon chlorine have been compelled to discontinue that process and to throw their hydrochloric acid into the market at any price. The manufacture of the acid from magnesium chloride will only come to the front again if soda-ash has become so cheap that the glassworks will find it more remunerative to employ this article than saltcake, or when new manufactures arise which are large consumers of hydrochloric acid.

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[1] *Loc. cit.*, p. 356.

[2] Th. Meyer, *loc. cit.*, p. 85.

The great purity of the hydrochloric acid made from magnesium chloride, the entire absence of sulphuric acid, arsenic, selenium, etc., will always secure for it a better price than that of ordinary muriatic acid.

D. *From Carnallite, etc.*

Solvay (Ger. P. 44865) treats carnallite, kainite, or a mixture of both, with or without addition of clay or magnesia, in a strong vacuum at 100° to 200° C., and if necessary with the assistance of strong mechanical pressure, to obtain a dry mass, from which at a red heat air liberates chlorine, or steam hydrochloric acid.

Kossman[1] points out that those of the above-mentioned processes in which $CaCl_2$ is added to $MgCl_2$ are not advantageous, because, according to thermochemical data, the removal of chlorine from $CaCl_2$ requires much more heat than from $MgCl_2$. Nor can additions of inert substances be recommended. Fusion or fritting of the salt is very injurious, but can be partially remedied by mechanical division. Apart from this mechanical obstacle to the complete decomposition of magnesium chloride, we must remember the circumstance observed by Carnelley and Walker[2] that a long-continued heating may produce polymerisation, which forms substances of very high specific heat, offering great resistance to further decomposition. Among chemical additions magnesia is undoubtedly the best.

E. *From Ammonium Chloride.*

There is a possibility that methods for the manufacture of hydrochloric acid from ammonium chloride may assume great technical importance if the scheme at present on hand to combine the manufacture of ammonium chloride with the fixation of nitrogen by the Haber process proves a success.

Mond has recommended the decomposition of ammonium chloride, obtained by crystallisation from the mother-liquors of the ammonia-soda manufacture, by sulphuric acid (B. Ps. 3820 and 3922, of 1883). The ammonium chloride is to be heated with twice its equivalent of sulphuric acid in iron or leaden pans to 120°, and the ammonium bisulphate formed is to be converted into neutral sulphate by ammonia vapour. The process is, of course, only applicable on a restricted scale, and has not been carried out to any large extent. According to further patents of Mond's (Nos. 65, 5238, 8308, of 1886, and others) the ammonium chloride is to be volatilised, and the dissociated vapours of NH_3 and HCl are to be conveyed over oxides of cobalt, nickel, iron, manganese, aluminium, copper, or magnesium, which retain the HCl. These patents were taken out for the production of hydrochloric acid as well as of chlorine, but they are evidently only intended for the latter.

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[1] *Loc. cit.*, p. 355.

[2] *J. Chem. Soc.*, 1888, 53, 59.

Gilloteaux (Ger P. 49503) heats ammonium chloride with sodium or ammonium bisulphate, whereby HCl is evolved and neutral sulphates are formed On heating the latter NH_3 is given off, the bisulphate is re-formed, and can be used over again The reactions are:—

1. $2NaHSO_4 + 2NH_4Cl \qquad 2HCl + (NH_4)_2SO_4 + Na_2SO_4$.
2. $(NH_4)_2SO_4 + Na_2SO_4 \qquad 2NH_3 + 2NaHSO_4$.

The first reaction is anything but complete, for which reason Mond's patent 3820, of 1883, stops at the conversion of NH_4Cl by H_2SO_4 into HCl and NH_4HSO_4. Indeed Mond[1] asserts that no reaction whatever takes place between ammonium bisulphate and ammonium chloride; below a certain temperature nothing occurs, and above that temperature sal-ammoniac is volatilised.

O. N. Witt (Ger. P. 34395) proposed converting ammonium chloride by syrupy phosphoric acid into HCl and ammonium phosphate. On further heating the latter gives up all NH_3, and leaves vitreous phosphoric acid behind, which is dissolved in water and used over again.

Jurisch,[2] after a number of laboratory experiments, comes to the conclusion that in this way indeed all HCl can be driven off from NH_4Cl, but only by means of an excess of phosphoric acid, which may certainly be used over again. Of the ammonia only 63·6 to 86·1 per cent. is recovered [which alone would make the process practically impossible]. Jurisch rightly observes that Witt's proposal cannot be utilised until a material for making furnaces and vessels is discovered which will resist fused phosphoric acid for any length of time. We do not at present know of any such material.

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[1] *J. Soc. Chem. Ind.*, 1884, p. 587.

[2] *Dingl. polyt. J.*, **267**, 431.

Whitehouse (Eng. P. 15140, of 1907) heats ammonium chloride, preferably though not necessarily in the dry state, to about 300° C. with one or more of the oxides or oxychlorides, of cerium, thorium, didymium, lanthanum, or yttrium, whereby ammonia is given off and chlorides of the earth or earths used are formed. The latter are then heated to 450° to 500° C. in air or steam to cause evolution of chlorine or hydrochloric acid, and regeneration of the rare earth or earths employed.

CHAPTER X

WEAK ACID; CONTROL OF CONDENSATION; YIELDS, COSTS, PURIFICATION, PUMPING AND CONVEYANCE OF HYDROCHLORIC ACID

THE control of the condensing-apparatus has two objects, viz., first, the completest possible condensation of all the HCl contained in the gas; secondly, the production of the largest possible quantity of *strong* acid. Although these aims are in some degree antagonistic, there is no reason why with a properly designed plant both objects should not be attained. The problem is simplified if weaker acid can be made, and this is usually done when the acid is to be used up at once in the works, but even in such cases the increased volume of the dilute acid has obvious disadvantages.

At most well-conducted works the post-condensers for blind roasters are now abolished. This has been done in England mainly by very greatly enlarging the stone towers, and elsewhere by placing a sufficient number of cisterns or receivers between the saltcake-furnaces and the tower. Thus the quantity of weak acid made has been very much diminished, and what remains is mostly employed for feeding the strong acid condensers.

Control of the Condensation.

This must take account both of the completeness of the removal of the HCl from the gases and of the strength of the acid. The acid running out of the condensers, tanks, or receivers ought to be strong enough for sale acid, that is in winter 34° to 36°, in summer 30° to 32° Tw.; for own use, acid of 23° to 2[illegible]° is frequently sufficient, but the higher strength is preferable. Sometimes samples are taken several times a day and tested by the hydrometer; but it is best to run all the acid coming from the condensing-apparatus through a glass cylinder in which a hydrometer floats, so that the strength of the acid can be seen without the time and trouble of sampling.

It should not be overlooked that hydrochloric acid cannot easily be obtained of the highest strength unless sulphuric acid of 140° or 144° Tw. is employed for decomposing; otherwise too much steam has to be condensed together with HCl.

Nor should it be forgotten that the hydrometer at a high temperature indicates much less strength than at a lower one; according to the table given on p. 45, an acid which at 15° shows 20° Tw., would only show 16° Tw. at 70°. Before testing, the acid must therefore be cooled down to the ordinary temperature.

Dr Angus Smith[1] gives a special instance of the condensing process as observed at a works at St Helens, decomposing daily 6 tons 12 cwt. of common salt, which ought to produce 76·16 cwt. of dry HCl or 253·88 cwt. of 30 per cent. acid of 31° Tw. It appears that there was a blind roaster, and that both pan- and roaster-gas passed into the same condenser. First they passed through a small cistern close to the furnace, in which in twenty-four hours about one third of a cubic foot of 27 per cent. acid was condensed; it was very impure, and its temperature was 46° C. In a second, more distant cistern in the same period 48·1 cub. ft. of 31 per cent. acid at 32° C collected; the condenser furnished in twenty-four hours 400 cub. ft. of 29 per cent. acid at 54°·5 C. The percentage of HCl and steam in the acid gases was twice examined, and found as follows (I. evidently during the most, II. during the least energetic evolution of gas):—

	Grms. H_2O in 1 cbm. of gas.	Grms. HCl in 1 cbm. of gas.
3 feet from the pan . . .	1109·2"	1511·99
Near the roaster . . .	44·35	304·53
On entering the condenser .	51·06	293·38

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[1] *Eleventh Report on the Alkali Acts*, p. 40.

II.

	Grms. H_2O in 1 cbm. of gas.	Grms. HCl in 1 cbm. of gas.
3 feet from the pan . . .	146·0	129·66
Near the roaster . . .	1·46	65·45
On entering the condenser . .	16·23	37·85

The temperature of the pan-gas was 180°, that of the roaster-gas 315° C., that of the gas entering the tower 60° C. In spite of this, only one-eighth of the HCl was condensed before reaching the tower, and the tower had to perform the other seven-eighths of the condensation.

The *regulation of the draught* is very important. There must be in the connecting flue a damper of glass, slate, stoneware, or lead, which is regulated so that the gas can just pass through but does not blow out of the working-doors of the furnaces. If more draught is given, uncondensed HCl gas inevitably gets into the chimney, even with an excess of water. In some works the damper is put under lock and key, because the furnace-men are apt to open it more widely in order to get more draught. Stoneware fans are often used in modern plants, and Messrs Kestner also make fans which give a suction if used after the absorption towers. In all well-conducted modern works, the final exit is placed at a low level where it is under ready and constant observation To put it up the chimney at the finish is likely to cause bad work or bad control to pass unnoticed.

If chimney draught is not available, the best method of obtaining a draught is by the "induced" system. A high pressure fan of ordinary construction blows air through one or other of two concentric tubes and causes a suction in the other. Only pure air passes through the fan which thus escapes corrosion. Even when chimney draught is available this system is worth using, since it enables one to have an exit which can be kept under constant observation.

The maximum allowable escape of gas has been already mentioned on p. 230. This is perhaps the most important point of all in control—certainly it is the most difficult. Several recorders have been devised to automatically measure and record the acidity of the escaping gas. The usual verdict on them is that they require the full-time attention of a competent chemist to keep them working. Such an automatic recorder is, however, undoubtedly possible, and when a reliable one arrives it will receive a cordial welcome. Even the continuous taking and measuring of samples is not quite easy. It is best done, according to Mactear, by a small gas-meter, which, in order to prevent corrosion of its parts, is placed *behind* the absorbing apparatus. But an ordinary aspirator of sufficiently large size will fulfil the same purpose in a cheaper way, and is less liable to get out of order. Kuhlmann Fils[1] proposes to measure the speed of the gases by evolving coloured vapours at the foot of the chimney, and observing the time which they take in getting to the top.

Usually, however, only a certain volume of gas is aspirated, first from the entrance-pipe and then from the exit-pipe of the gases, and the proportion of HCl in both is estimated. For aspirating, the Alkali Inspectors employ small finger-pumps made of indiarubber balls, which on compression give up nearly constant quantities of air. Standing aspirators are preferable. A very simple and cheap apparatus of this kind is represented in Fig. 139. It consists of two glass bottles, I. and II., say "Winchester quarts," provided with a twice-perforated cork or indiarubber stopper, through which passes one elbow-tube ending just below it, and another reaching down to its bottom. We will call the former *a* and *b*, the latter *c* and *d*. The tubes *c* and *d* are connected by an elastic tube; another elastic tube connects either *a* or *b* with the apparatus through which the gas is to be aspirated—say, with a small Woulfe's bottle containing water and connected also with the outlet of the condenser. One of the bottles, say I., is placed so that its bottom is raised above the neck of II. If, now, *b* is connected with the absorbing apparatus, and the air is sucked from *a* for a moment, the siphon formed by *c d* and the elastic tube begins to run, whilst gas is aspirated from *b*. When the contents of I. are run out, the elastic tube is detached from *b*, the position of the bottles is changed, so that II. now stands higher, and the elastic tube is put upon *a*; the connection between *c* and *d* is not touched. If the attendant sucks for a moment at *b*, the apparatus starts working again. Usually sufficient water remains in the tube *b* in the shape of beads to make the siphon start of its own accord. The quantity of water running out of the bottles, independent of that always remaining at the bottom, is determined once for all, or a more exact scale can be put upon the bottles themselves.

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[1] *Année Industrielle*, 1878, p. 67.

For absorbing the acid-gases, either distilled water, or weak soda solution, or a measured quantity of standard silver solution is employed. In the last case, the unused silver nitrate may be determined with a standard solution of ammonium thiocyanate; in the former cases the chloride may be titrated with standard silver nitrate, with chromate as indicator, if the sulphur dioxide is first oxidised. Some SO_2 is always present, not only in the fire-gases, but also in the condenser-gas not mixed with fire-gas, probably from the action of sulphuric acid vapour upon the

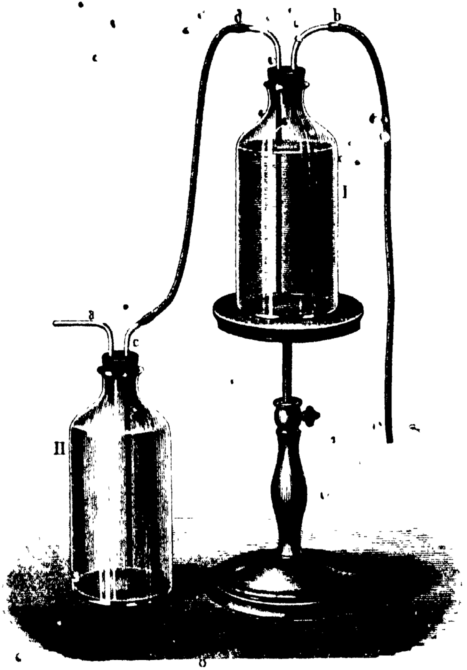

Fig. 139.

coke. Even small quantities of SO_2 make Mohr's process impossible for direct use. But it can be employed if to the liquid a diluted solution of permanganate is carefully added till the pink colour just appears. All the SO_2 is now oxidised to H_2SO_4; the liquid is neutralised with soda, a very slight excess of which does no harm, no more than the extremely small excess of permanganate. Potassium chromate is added, and the liquid titrated with standard nitrate of silver.

As *indicator* for the exit-gases from acid-works, Mr Ballard recommends metanil-yellow, which is slowly bleached by chlorine or SO_2, but with HCl yields a heliotrope tint.

For the titration of solutions which have a slightly yellow colour to begin with, Kirschnick[1] employs a mixture of methyl-orange and sodium indigo-sulphonate. Dissolve 1 g. of each of these substances separately in a litre of water each, mix 20 c.c. of the first and 60 c.c. of the second solution and dilute the mixture to 1000 c.c. Of the solution thus obtained employ 10 c.c. as indicator for each titration. Basic substances produce a green colour, acid substances pink. Luther[2] confirms this and adds the statement that this mixed indicator is also very useful for the titration of liquids containing carbonates, in which case the CO_2 produces an almost neutral grey, hardly at all perceptible in dilute solutions, which is taken as the final point. Since the succession of colours is from yellow through green to grey (or colourless) and then to purple, the operator is prepared for the final point and more easily avoids exceeding it.

Frequently, and in Great Britain always, in consequence of the requirements of the law, the task imposed upon the chemist is to test the exit-gases not merely for HCl but also for their *total acidity*. In this case it is not practicable to pass the gases through titrated solutions of sodium carbonate or hydrate and to retitrate them after addition of methyl-orange, since this indicator is affected by SO_2 differently from HCl and H_2SO_4. On the other hand, phenolphthalein has the drawback of being affected by CO_2 as well, which may frequently cause grave errors. But it is not necessary to renounce the use of methyl-orange, when following the process employed by the British Alkali Inspectors, who pass the gases through a solution of pure hydrogen peroxide (free from HCl) in pure water. Thus the SO_2 is quantitatively oxidised to H_2SO_4. When adding methyl-orange and retitrating with standard solution of sodium hydrate or carbonate, the total acidity is found, thereupon potassium chromate is added, and the chloride is titrated with silver nitrate.

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[1] *Chem. Zeit.*, 1907, p. 960.

[2] *Chem. Zeit.*, 1907, p. 1172.

In many cases this can be done quite easily, but very frequently it happens that when titrating with silver nitrate, a black or green precipitate is produced which altogether interferes with the well-known red colour of the silver chromate. Such "black" or "green" tests occur in establishments of any kind where salt is decomposed, but more particularly in the exit-gases from copper-extraction works. Carpenter and Linder, in the *Thirty-fifth Report on Alkali Works*, for 1898, state their experiences in this matter. Those colours are caused by the reduction of silver solution, probably to a mixture of Ag_2O and Ag, which possesses a bluish-black tint. The reduction may be caused by organic substances contained in the chimney gases which escape the oxidisation by hydrogen peroxide. The following overcomes this difficulty. After determining as above the total acidity, calculated as SO_3, by titration with soda solution, add about 0·5 g. calcium or magnesium carbonate and afterwards 5 to 10 drops of a 5 per cent. ferrous sulphate solution, agitate for a minute, decant or filter, and titrate the solution as usual with potassium chromate and silver nitrate. The precipitate of ferrous carbonate formed in that process carries down all the organic substance, and in the solution filtered from it the hydrogen peroxide does not act as a reducing agent on argentic nitrate, but is quite harmless.

If the question is merely to estimate the HCl, it was formerly considered sufficient to pass the gases through water, to oxidise the SO_2 by potassium permanganate, neutralise with sodium carbonate and titrate with potassium chromate and silver nitrate, as above. But in this process also "green" or "black" tests occur, since the manganous sulphate, formed by the action of SO_2, reduces some silver nitrate. This can be avoided, if after adding the potassium permanganate a mixture of ground chalk and potassium bichromate is used, but it is simpler to replace the permanganate by hydrogen peroxide, in which case the difficulties just mentioned do not occur.

To ensure complete absorption of the smallest quantity of HCl in the large volume of gas, a simple bubbling of the gas through the liquid contained in a Woulfe's bottle is not sufficient; a larger surface of contact between gas and water must be produced. This is very well done, for instance, by the small apparatus shown in Fig. 140, and first introduced by Mr Glendinning. The gas enters at *a* as usual; it leaves the bottles through the wider tube *b*, which is connected with the aspirator at *c*; *b* is blown into a bulb at the bottom; and a number of small holes are made in that bulb. The whole tube is filled with broken glass. It is put down just to the level of the liquid. The current of gas carries some liquid through the fine holes into *b* where the gas and water are mixed into froth by the broken glass and come into intimate contact. The tube *b* should be pretty long, as the liquid is sucked up into it to a considerable height. For the perforated glass ball an open glass tube, closed by a cork with fine longitudinal nicks, may be substituted.

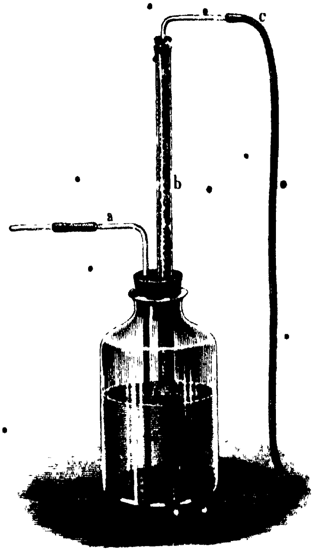

FIG. 140.

Taking the Samples.—In order to take the samples, there must be 1-in. holes drilled in suitable places of the gas-pipes of course usually closed in some way. For testing, a cork is put in which contains a glass tube reaching to one-third of the radius of the gas-flue, and so placed that no drops of liquid can fall into it. This tube is connected outside with the absorbing apparatus, and the latter with the aspirator.

Jurisch[1] has made a number of experiments which prove that the assumption, according to which the velocity of a gaseous current at a distance of one-third of the radius from the periphery of the pipe or flue is equal to the mean velocity of the whole current, leads to errors between the limits of −3 and +30 per cent., in the case either of horizontal, upward, or downward currents, lead pipes, earthenware pipes, or brick chimneys. For exact measurements a number of tests must be taken at different points of the radius. Unfortunately, Jurisch gives no hint how, from these various tests, the mean velocity or the real composition of the gas is to be deduced, and we shall therefore be constrained to adhere to the usual method, which at any rate yields results sufficiently accurate for comparison.

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[1] *Chem. Ind.*, 1893, p. 425.

In the Hargreaves process some salt is always carried away mechanically by the draught in the moulding and drying apparatus. This would affect the results of the chimney-test for chlorides, unless the salt were kept out. Mr Fletcher, as stated in the *Alkali Inspectors' Report*, 1877-78, p. 76, found that this could be done by filtering the gas through asbestos, which at temperatures above 100° C. does not retain any HCl. Glass wool, on the contrary, retained some acid, probably by its alkaline constituents.[1]

The *Committee of Alkali-makers* in 1881 gave the following *rules for the testing of hydrochloric acid escapes*:—A continuous test over twenty-four hours in one chimney, with intermittent daily bellows test at nine o'clock, or other specified time, to be taken and recorded; particulars of the work done by the chimney to be given, viz., quantity of fuel-gases passing into it, whether close or open roasters are used, and any other particulars that may be desirable. The observing-apparatus to consist of three bottles or tubes containing not less than 100 c.c. of absorbing liquid, a depth of 3 in. in each. The aperture of the inlet-tube not to exceed $\frac{1}{32}$ of an inch in diameter, and of the second and third $\frac{1}{80}$. Wires for the purpose of measuring this will be supplied by Mr Muspratt. Absorbing-liquid: distilled water free from chloride. Speed of aspiration as near as possible ½ cub. ft. per hour. Mode of testing: decinormal nitrate of silver (10·8 Ag per litre), and "chromate indicator." The intermittent test, above alluded to, to be made with bellows at a stated hour, and once daily, but at such time as the escape of hydrochloric acid may be expected to be greatest. Temperature and barometric pressure: the variations of these to be noted, and corrections made to 30 in. bar. and 60° F. The results to be stated in grains per cubic foot.

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[1] *Cf.* Davis, *J. Soc. Chem. Ind.*, 1882, p. 375.

The above rules do not take into account that the chromate indicator does not act when (as is frequently the case) SO_2 occurs in the gas; but we have seen (p. 372) that this can be remedied by oxidising the SO_2 by means of permanganate.

For apparatus for testing the exit-gases from acid towers, reference may be made to the papers of Lovett,[1] Pringle,[2] and Davis,[3] which give descriptions of testing-apparatus actually in use, and to Lunge's *Technical Chemists' Handbook*, 1916, p. 149.

The latest contribution to this subject has been made by G. Kohn.[4] If a highly diluted gas passes through a series of towers under equal conditions, the proportion between the total quantity of absorbable gas and that actually absorbed will be the same in all towers. Hence, if we ascertain the quantity of gas absorbed in each tower, we can calculate the quantity of gas not yet absorbed. Let us call a, b, c, the number of kilograms of gas absorbed in towers a, b, c; z the kilograms of gas leaving tower c unabsorbed. Then is

$$a : b : c = (a+b+c+z) : (b+c+z) : (c+z)$$

or

$$\frac{a}{a+b+c+z} = \frac{b}{b+c+z} = \frac{c}{c+z}$$

and

$$bx = (b+c+z) : (c+z);\ z = \frac{c^2}{b-c}.$$

In practice absolutely equal conditions of absorption are not attainable, and not even desirable, but the formula allows of drawing conclusions on the possibility of improvements. If we call the proportion of the absorbed to the total quantity of the gas to be absorbed in each tower $\frac{p}{q}$, and s the total quantity of this gas, then is

$$a = \frac{sp}{q};\ b = \frac{sp}{q} \times \frac{q-p}{q};\ a : b = 1 : \frac{q-p}{q};\ \text{and}\ \frac{p}{q} = \frac{a-b}{a}.$$

$$\text{Also}\quad \frac{p}{q} = \frac{b-c}{b},\ \text{therefore}\ b^2 = ac.$$

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[1] *J. Soc. Chem. Ind.*, 1882, p. 210.

[2] *Ibid.*, 1883, p. 58.

[3] *Chem. News*, 41, 188.

[4] *Chem. Zeit.*, 1907, p. 758.

The yield should approximately correspond to this equation. The value $\frac{p}{q}$ is independent of the total quantity to be absorbed.

On applying these principles to a series of three towers, the average value of x was found $= 8·3$ per cent., and in reality the loss by the exit-gases was very nearly equal to this, viz., 9·1 per cent.

The reports of the inspectors under the Alkali Acts show the actual state of affairs with respect to the escape of HCl at the English and Irish factories. For the years up to 1901 we refer to the previous editions of this treatise; and we shall here merely quote the figures for the average escape of acid-gases from 1902 onward, including some interesting statements from other manufactures. For the years 1905 to 1907 the Scottish works are included in the above. In the original the figures are given also for each district separately, and are given in grains per cubic foot, but we have also recalculated them for grammes per cubic metre :—

	1902	1903.	1904	1905	1906.	1907.
Number of saltcake-works, registered	51	47	43	54	56	54
" cylinder muriatic-acid works	16	16	17	19	20	18
" sulphuric-acid works . .	171	169	168	192	190	277
" chemical-manure works .	178	173	169	211	208	207
HCl in chimney gases of alkali-works,						
grains per cubic foot . . .	0·086	0·089	0·081	0·083	0·082	0·082
= grammes per cubic metre .	0·196	0·187	0·185	0·191	0·189	0·189
per cent. of total HCl produced	98·59	98·47	98·69	98·52	98·22	98·31
Acid-gases escaping from sulphuric-acid chambers, given as SO_3,						
grains per cubic foot . . .	1·216	1·248	1·191	1·227	1·197	1·145
= grammes per cubic metre .	2·781	2·854	2·724	2·802	2·753	2·619
Acidity of gases of all chimneys, as SO_3,						
grains per cubic foot . . .	0·706	0·728	0·775	0·793	0·737	1·044
= grammes per cubic metre .	1·614	1·628	1·772	1·824	1·695	2·388
Acidity of gases from condensers of manure-works, as the SO_3 equivalent of H_2SiF_6,						
grains per cubic foot . . .	0·325	0·244	0·228	0·228	0·214	0·202
= grammes per cubic metre .	0·743	0·558	0·521	0·521	0·492	0·462

Under the Alkali, &c., Works Regulation Act, 1906, which came into force on the 1st Jan. 1907, the Alkali Acts of 1881 and 1892 were entirely repealed and many new regulations introduced. Among the main points of difference the following may be noted:—

Chlorine Works.—The definition is extended to works in which chlorine is used in any process.

Muriatic Acid Works now includes any works (other than alkali works) where hydrochloric acid is evolved in any manufacturing operation whatsoever.

The term "alkali-works" from 1907 onwards comprises every work for—

(*a*) The manufacture of sulphate of soda or sulphate of potash, or

(*b*) The treatment of copper ores by common salt, or other chlorides, whereby any sulphate is formed,

in which muriatic gas is evolved.

The table on p. 380 is drawn up from the Annual Reports on Alkali Works.

Yields.

The results of working the condensers have been mentioned several times before, particularly the unsatisfactory results obtained with the older condensers. Few works possess any contrivances for exactly measuring the acid produced; only where all of it is sold can a complete check be obtained. So much is certain, that with really good condensing-apparatus by far the largest portion of the HCl given off can be recovered. Theoretically 100 parts of NaCl would yield $\frac{36{\cdot}46 \times 100}{58{\cdot}5} = 62{\cdot}32$ dry HCl, or expressed in acid of 34° Tw. (= 32·3 per cent. HCl at 0° C.), 193 parts of such by weight, or nearly 165 litres for 100 kg. pure NaCl, = 368 gallons per ton. Common salt of 93 per cent. would theoretically yield 179·5 kg. (or 153·3 litres at 0° C.) of the above acid, = 343 gallons.

On calculating the acid to be obtained per ton, not merely the percentage of the common salt employed, but also the NaCl left in the saltcake must, of course, be taken into account, which reduces the amount of acid obtainable.

Of the many statements of the *actual* yield of hydrochloric acid, only a few need be repeated here. H. Allhusen[1]

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[1] *Richardson and Watts*, 6, 235.

	1904	1905	1906	1907	1908	1909	1910	1911	1912	1913	1914	1915	1916	1917	1918	1919	1920
Number of saltcake-works	43	45	48	47	49	51	50	50	48	48	47	45	44	43	54	57	46
Number of cylinder muriatic-acid works	17	17	16	15	15	13	13	13	14	12	11	10	11	11			
Number of muriatic-acid works (other than alkali-works) .	...	41	43	46	51	54	55	58	56	63	65	63	62	66	69	66	77
HCl in chimney gases in alkali-works (grains per cubic foot) .	0.081	0·083	0·082	0·082	0·073	0·070	0·071	0·076	0·076	0·076	0·076	0·074	0·086	0·089	0·076	0·078	0·088
HCl. Amount condensed in alkali-works compared with that produced per cent. . . .	98.69	98·52	98·22	98·31	98·39	98·76	98·97	98·69	98·74	98·81	98·49	98·34	97·90	97·81	98·00	98·41	98·5
HCl in chimney gases in muriatic-acid works. Grains per cubic foot . .	0.057	0.049	0·055	0·049	0·059	0·053	0·053	0·055	0·040	0·059	0·049	0·036	0·034	0·029	0·023	0·031	0·061

states the result of six accurate trials on the large scale as follows:—

68·60	per cent. of the theoretical yield from the	pan-gas.
29·40	" " "	roaster-gas.
2·00	" loss.	

Clapham[1] states as the result of six months' accurate observation:—

100 parts of common salt yielded . . .	55·80 HCl
Left in the sulphate	1·52 "
Loss	0·58 "
Possible yield	57·90 "

At Messrs Garrett's of Wigan, there were condensed:—

In the stone cisterns	66·04 per cent.
" receivers following them . .	33·396 "
" coke-tower	0·562 "
Found in the gas leaving the latter .	0·002 "
	100·000 "

This, however, only refers to the HCl found by analysis, and takes no account of losses by leakage, etc.

According to Schrader (*loc. cit.*), from 92 per cent. salt as much as 145 parts of acid of 34° to 36° Tw. can be actually obtained, instead of 175·9 parts by theory; according to Payen, 120 to 125 parts instead of 154·7; according to Balard,[2] at Chauny 95 per cent. are recovered, viz., 150 parts acid of 21° Bé. (34° Tw.) to 100 parts salt containing from 5 to 6 per cent. water.

The following figures were supplied by a German works:—(*a*) 133 parts acid of 21° Bé. (= 32° Tw.) from 100 parts of a mixture of 72 rock-salt and 28 nitre-cake; (*b*) 140 to 150 parts of acid of 20° Bé. from 100 parts of common salt. At Aussig, where the very pure salt of Neu-Stassfurt (which contains 99 per cent. NaCl, and yields 120 per cent. of sulphate) is employed, a yield of 148 parts of hydrochloric acid of 34° to 36° Tw. is obtained from 100 parts of saltcake, or 170 parts from 100 parts of salt. At one of the foremost German works they obtained in 1884, 180 parts acid of 20° Bé. (sp. gr. 1·163) from 100 parts of best common salt. This would be equal to nearly 173 parts acid of 34° Tw.

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[1] *Richardson and Watts*, 6, 260.

[2] *Rapport du Jury International*, 1867, 7, 45.

The yield of acid from mechanical furnaces has been mentioned, pp. 145 and 151.

A German works employing "plate-columns" ("Lunge towers") obtains from 100 parts of 99 per cent. rock-salt a yield of 183·2 parts acid of 20° Bé., which is superior to any of the above-mentioned cases.

Costs of Plant and Working of a Saltcake and Muriatic-Acid Works.

We quote these from Th. Meyer,[1] as referring to a production of 2100 tons of muriatic acid of 20° Bé. (= 32½° Tw.) and of 1485 tons saltcake.

A. *Cost of Plant.*

	Mark.*
Ground space	5,000
Buildings	15,000
Muffle-furnace and decomposing-pan . .	9,500
Preliminary cooler . . .	2,800
Condensers and final tower	6,700
Staging, supports, etc.	3,000
	40,000

B. *Working Expenses (per annum).*

1235 tons rock-salt, 97·5 per cent. .	at M.	1·20 =	14,820
1275 „ sulphuric acid, 1·7 sp. gr.	„	2·00 =	25,500
62 „ nitre-cake for denaturing the salt	„	1·00 =	620
445 „ coal	„	1·70 =	7,565
Small stores, lighting			1,000
Repairs			3,500
Wages: 330 working days, 5 men .	„	4·00 =	6,600
Foreman (manager)			3,000
Interest on cost of plant, 4 per cent. on 40,000 mark			1,600
Depreciation of buildings, 5 per cent. on 15,000 „			750
„ plant, 10 per cent. on 25,000 „			2,500
			67,455

*£1 = 28·84 mark.

Assuming the 1485 tons of saltcake to fetch a price of 2·80 mark per ton—that is, 41,580 mark—this leaves for the 2100 tons muriatic acid (32½° Tw.) a cost of 25,875, or 1·23 mark per 100-kg. (say, 12s. 0½d. per ton), exclusive of general expenses.

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[1] *Fabr. v. Sulfat und Salzsaure*, 1907, p. 77.

Pumping Hydrochloric Acid.

Formerly, whenever it was proposed to lay out an alkali-works, the very first requirement to be fulfilled was to take care that no pumping of hydrochloric acid should take place on any account. Even the weak acid from post-condensers was only pumped up at a very few places for feeding the strong condensers, because the pumping contrivances then known were very defective, and were frequently abandoned even where they had been working for some time.

Nowadays the position of matters is quite different. Stoneware pumps, which were formerly almost regarded as playthings, are now made of quite a serviceable kind; and stoneware is made strong enough even to serve for "acid eggs." Instead of the easily melted gutta-percha, ebonite is employed. Even acid-resisting metallic alloys are known and employed. The "membrane-pumps" afford a means of altogether avoiding the contact of acid with metals.

The difficulty at present consists in deciding which of the many contrivances to choose for pumping hydrochloric acid, but nobody need now shrink from raising not merely weak but also strong acid to any desired height. For good reasons this will even now, if possible, be avoided in the case of strong acid, and it is always preferable to lay out the condensing-plant in such manner that there is a natural fall for the acid to be used or sold; but it is very fortunate that this is no longer imperatively required, and that even strong acid can be pumped, which is especially important in the case of changes of plant. Weak acid is nowadays pumped without any hesitation, probably in the majority of works.

We shall now describe the various plans for raising hydrochloric acid.

Force pumps can be constructed from acid-proof stoneware, or from metal with acid-proof lining, or entirely from acid-proof alloys of metals. We show here the stoneware pumps of Doulton & Co., of Lambeth (Fig. 141), and those of the Deutsche Ton- und Steinzeugwerke of Charlottenburg (Fig. 142). The latter has the advantage that the valve-seats are easily accessible; the valves consist of indiarubber balls (for nitric acid of stoneware). The packing washers consist of india-rubber or asbestos, and the application of screw-fastenings, which in the case of a fragile material like stoneware, is always a source of weakness, is reduced to a minimum.

A very similarly constructed pump, made of a peculiar white metallic alloy, according to Hargreaves and Robinson's patent, is made by W. H. Bailey & Co., Salford, and is employed by many manufacturers. It is shown in Fig. 143.

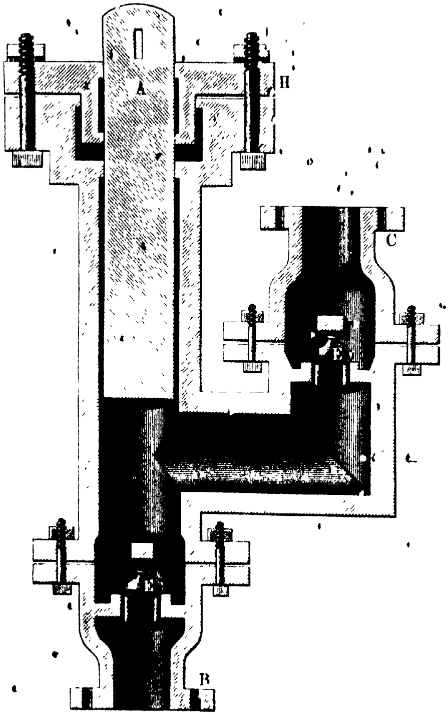

FIG. 141.

Metallic pumps, with ebonite lining and other parts, also similar in principle to those shown here, are built by L. G. Dehne, of Halle (Prussian Saxony).

Another kind of pump, in which the moving parts do not come into contact with the liquids, but impart the motion to it

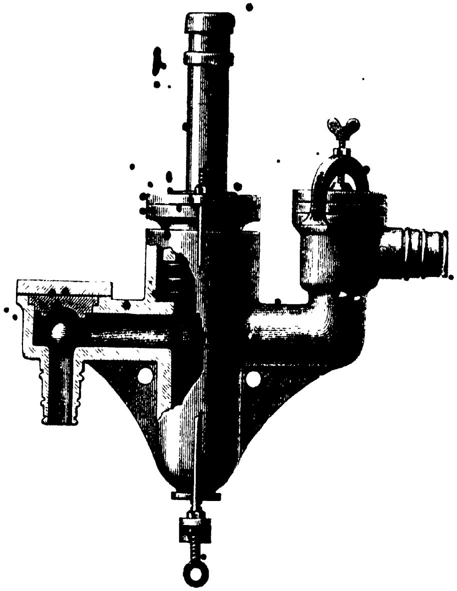

FIG. 142.

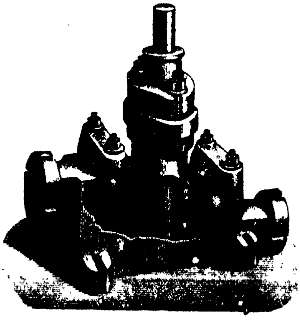

FIG. 143.

by a flexible membrane, is called a "*membrane-pump.*" These pumps have been patented in Britain by Hazelhurst (1957, of 1874; 150 and 2527, of 1876), and are shown in Fig. 144.

A A′ is an ordinary pump-barrel; B B′ are two cast-iron saucers; C, an indiarubber diaphragm, separating the two saucers so that neither liquid nor air can pass from one side of the diaphragm to the other. D D are indiarubber ball-valves, the lower one for the acid suction-pipe, the upper one for the delivery-pipe. E is a water-cistern, communicating by F with

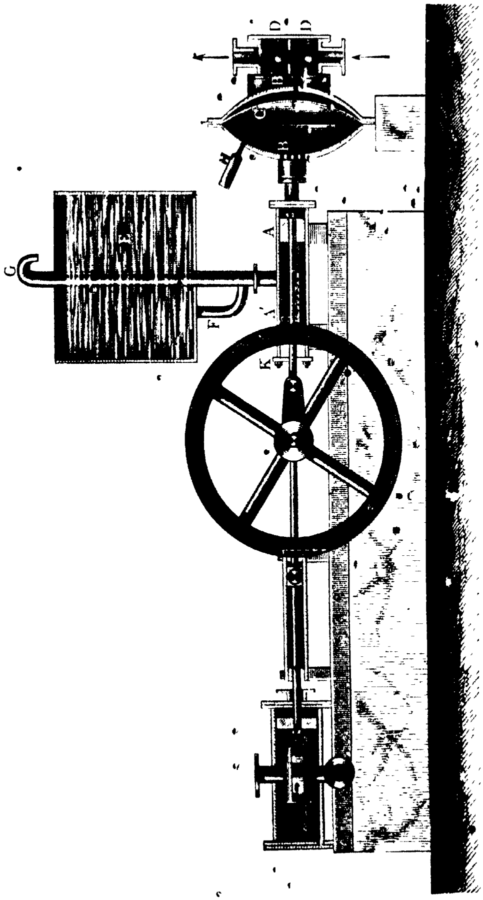

FIG. 144.

the side A′ of the pump-barrel. When the pump is set in motion, the diaphragm C waves to and fro, drawing and forcing the acid through the valves D D. At each *back* stroke the water in A′ shoots up the pipe G and is delivered into the top of E; at each *forward* stroke the water fills A′ from the bottom of the cistern through F. Thus the water is constantly changed without any valves whatsoever, avoiding the drawback caused by the inevitable entanglement of air passing through the gland K. The acid feed-cistern may be placed either below or above the pump; in the latter case an air-vessel is required on the suction-pipe. All parts requiring it are lined with indiarubber (or might be made of earthenware). This pump is specially intended for pumping back the weak acid to the strong acid, and it is employed successfully at many works.

Other descriptions of membrane-pumps are employed elsewhere, the parts in contact with acid being formed of acid-proof bronze, of an alloy of lead and antimony (which in many cases does not answer), or of ebonite. E. Haussmann, of Magdeburg, supplies membrane-pumps without pistons, actuated directly by steam.

Among simple metals *antimony*, especially when very pure, is the only one which resists both cold and moderately hot hydrochloric acid or its vapour. Hargreaves and Robinson (B. P. 5809, of 1882) patented the use of this metal for cooling-pipes, evaporating pans, and other apparatus serving for the treatment of hydrochloric acid. Later on, Mond proposed it for use with ammonium chloride, which comes to the same thing. For pumps, etc., antimony, owing to its brittleness, cannot be employed, but may be used for lining acid-eggs, etc.

Acid-proof bronze, according to Débié,[1] can be made of 15 parts copper, 2·34 zinc, 1·82 lead, and 1·1 antimony.

Wordsworth and Wolstenholme (B. P. 1429, of 1882) employ an indiarubber bag, contained in a chamber which it almost entirely fills on expanding. Both the bag and the chamber are accessible by separate pipes. The acid to be raised is admitted into the chamber, whereupon water is forced into the bag, so that the acid is forced out of the chamber into the pipes intended to convey it away. Or else the acid is put into the bag and the water outside.

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[1] *Polyt. Notizbl.*, 1888, p. 136.

A very peculiar and very ingeniously contrived pump, devised by Schlotter for strong hydrochloric acid, was described in the first edition, Vol. II., p. 258, and illustrated by large diagrams. It consists of several 1-in. glass tubes, coupled together in a frame, dipping into an acid jar, which are jerked upwards and take acid along by frictional resistance. As they are fragile and do not perform much work, they seem to have gone out again, and will not be described in detail here.

Centrifugal pumps, made of stoneware, by the Deutsche Ton- und Steinzeugwerke of Charlottenburg (Ger. Ps. 154525 and 231723) are constructed to lift large quantities, up to 5000 cub. ft. per hour, of acid liquids to moderate heights. Very favourable reports on these are made by Schulze-Pillot[1] and Plath.[2]

The application of *compressed air*, quite general for pumping sulphuric acid in "acid-eggs," was tried also for hydrochloric acid many years ago, but at first in an imperfect form. In the first edition, Vol. II., p. 252 *et seq.*, Clapham's apparatus, consisting of an acid-egg lined with gutta-percha, is described and illustrated. This apparatus was not employed except at the works managed by the inventor himself, because it was too troublesome to cool down all the acid and needed incessant repairs. Nowadays these drawbacks could be avoided by employing ebonite-lined acid-eggs, or those made of stoneware, like that shown in Fig. 146.

A more recent shape of these automatic eggs is described in the *Z. angew. Chem.*, 1907, p. 1187. Fig. 145 shows the connecting-pipe *c*, acid-egg *e*, rising-main *b*, entrance pipe for the liquid *i*, valve for the escape of air *a*. The ball-float *d* has two seats, one of these in cup *l*, whereby the air, entering through *h*, is shut off, and the other at *a*, which prevents the liquid from flowing back while rising in *b*. In the first instance *a* is open, as the ball-float *d* by its gravity rests on *a*; liquid enters *i* and fills *e*. When the valve-box has also been fitted with liquid, ball *d*, being hollow, rises from its seat, whereupon compressed air enters and forces it against *a*. Now no gas can get out at *a*; the air, therefore, presses downwards and forces the liquid from *n* and the acid-egg *e*, through the rising-main *b*, filling also the T-piece *c*. When *e* has been emptied to the point that air begins to escape through *h*, the liquid column *c* at once exerts its weight and forces *d* down upon *f*. Liquid from *i* then enters again into *e*, and the cycle begins over again. The principal advantage of this apparatus is its entire independence from the specific gravity of the liquid, and the restriction of moving parts to two balls which can be always replaced when broken.

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[1] *Z. angew. Chem.*, 1906, p. 420.

[2] *Ibid.*, 1907, p. 444.

Angerstein (Ger. P. 23731) uses an earthenware pot inside an iron one, and if necessary fills the intermediate space with pitch.

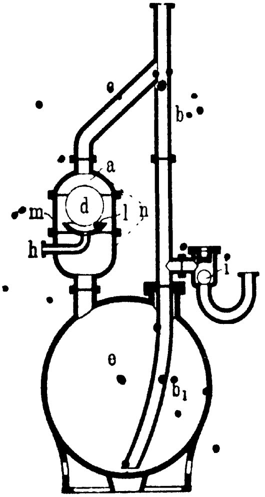


FIG. 145.

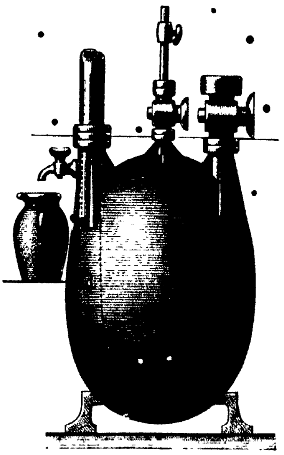


FIG. 146.

The Deutsche Ton- und Steinzeugwerke of Charlottenburg supply stoneware acid-eggs up to a capacity of 450 gallons, if intended for a pressure not exceeding one atmosphere, also eggs allowing a pressure of four atmospheres, but holding only from 20 to 30 gallons.

Wimpf and Schmid (Ger. P. 45729) employ an earthenware vessel, A, Fig. 147, tested to a pressure of five atmospheres, placed in the acid-cistern itself. In the lowest part of the conical bottom, *a a*, there is a hole, closed by a ball-valve, *k*. *r* is the pipe for compressed air; *r′* the rising main, closed by the ball-valve *k*. In the pipe *r*, between the vessel A and the air-pump, there is an enlargement *c*, filled by an elastic bag *b* (*cf.* the similar contrivance of Wordsworth and Wolstenholme, p. 387). This bag completely protects the air-pump against the acid vapours in A. When the air-pump is working, it merely compresses the elastic bag, whereupon a certain quantity of acid rises through *i*, *k'*, and *r'*; when the air-piston goes back, *k* opens, acid enters from without, and the bag *b* is again expanded.

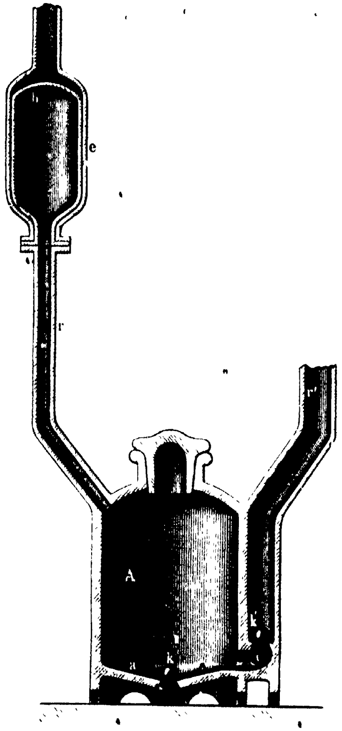


FIG. 147.

Instead of the ordinary way of employing compressed air, the *pulsometer principle*, which works automatically and without taps, can be advantageously employed. Fig. 148 shows an apparatus on this principle, constructed by P. Kestner.

The illustration clearly indicates the extreme simplicity of the mechanism, all the parts of which are strong and reliable in operation. The liquid contained in the feed tank A runs by gravity into the cylindrical body B of the acid elevator. As soon as the body is full, the acid operates the part X of the float which, by means of the rod C closes the air exhaust valve and opens the compressed air valve. The liquid is discharged through the pipe T, and the air, after delivering the liquid, exhausts through the same pipe, causing a fall of pressure in the apparatus which operates the valves in the opposite direction. This cycle being then repeated. It will be

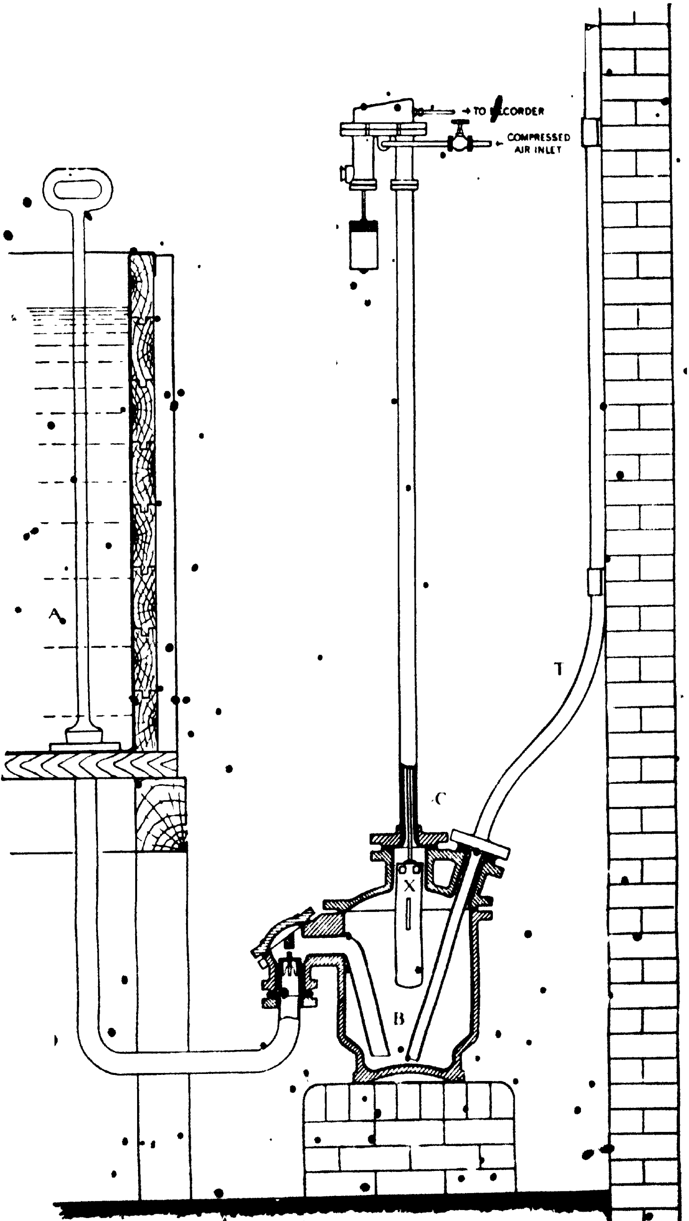


FIG. 148.

observed that there is no check valve on the delivery pipe; this is a very important point, as it simplifies the apparatus and, consequently, reduces maintenance charges.

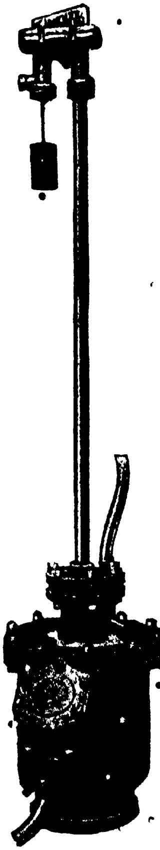


FIG. 149.

For elevating hydrochloric acid these elevators are lined throughout all parts with ebonite. In one form an earthenware body is used, in another a cast-iron body lined with ebonite.

For success in working, the elevator pipe should be run vertically upwards to the maximum height desired and the pipe then run with a downward fall in the desired direction. The external appearance of the Kestner elevator is shown in Fig. 149.

Special mention may be made of the *acid-pipe connection* employed with very great success at Aussig, and apparently superior for pumping-pipes to the ordinary systems. Instead of cementing and stemming, the joints are made by an india-rubber ring put round the spigot end of one earthenware pipe which is put into the faucet end of the next pipe with a certain degree of friction. This joint is not only perfectly tight, but gives to the whole length a certain degree of flexibility. The pipes themselves may be made of earthenware or even of glass.

Purification of Commercial Hydrochloric Acid.

The impurities of crude muriatic acid have been enumerated on p. 65. Non-volatile impurities can be removed from the acid most easily by distilling it with the usual precaution of rejecting the first and the last portions of the distillate. Ferric chloride passes over towards the end of the distillation. It can be retained by adding phosphoric acid but not by adding zinc or stannous chloride (to reduce it to $FeCl_2$).

Purification from Sulphuric Acid.—Very frequently hydrochloric acid is wanted almost entirely *free from sulphuric acia e.g.* for purifying the spent animal charcoal of sugar-works Hydrochloric acid containing but little sulphuric acid is alsc desirable for the manufacture of chlorine by the Weldon process and even more by the Deacon process.

During the course of the manufacture the pan-acid, which contains but little sulphuric acid, can be kept separate from the roaster-acid, containing more of it. In the Deacon process formerly only the former was employed, and the latter was utilised at the same works by the Weldon process. We must, however, first consider the case where the acid must contain even less sulphuric acid than is contained in ordinary pan-acid, and that in which the roaster-acid is required to be brought to the same state of purity.

A practically complete removal of the sulphuric acid from hydrochloric acid can be brought about by a careful addition of a solution of *barium chloride*. This has been known and practised for very many years past, *e.g.* for the acid sold to sugar-works for purifying the "char"; it was, notwithstanding, again patented by Wigg (B. P. 1220, of 1882).

It is rarely required that *roaster-acid* should be purified to the degree of being saleable as perfectly pure acid, but it is frequently desired to make it similar in quality to ordinary pan-acid. This can be done to some extent in the operation of condensing it. It is mentioned several times in Chap. VII. that by the application of a "preliminary tower" a great part of the sulphuric acid can be kept back by employing in this tower just sufficient water to retain the sulphuric acid, but very little HCl. It is, however, impracticable entirely to exclude the sulphuric acid by that means, since the gases mostly contain sulphuric anhydride, which is with difficulty completely absorbed by passing over water, so that sometimes in the last receivers of a series more sulphuric acid is found than in the first.

In well-managed works the pan-acid contains from $\frac{1}{8}$ to $\frac{1}{4}$ per cent., the roaster-acid $\frac{3}{4}$ to 1 per cent. SO_3, but even up to 2 per cent. SO_3 may be found in the latter.

In the manufacture of chlorine with native manganese, the sulphuric acid contained in roaster-acid is hardly injurious at all; it simply replaces its equivalent of HCl, and forms $MnSO_4$. In the Weldon process, however, it is inconvenient, since it forms with the calcium chloride a precipitate of calcium sulphate which in the neutralising wells increases the quantity of mud, and caused much loss of manganese compounds in the recovery, until it was properly understood how this mud can be deprived of its soluble portions by methodical washing or by filter-presses. In order to prevent this source of loss, Weldon and Stripe (B. P. 222, of 1881) treat the roaster-acid before use with part of the calcium chloride solution running to waste in the Weldon process, and separate the clear acid from the precipitate formed.

Sulphuric acid is much more injurious in the Deacon process, than in the Weldon process. For this reason for many years only the pan-acid was available for this process, and the roaster-acid had to be disposed of elsewhere. This great drawback of course called forth various proposals for purifying the roaster-acid, some of which gave at the same time a mixture of HCl vapour with air, suitable for the Deacon process.

In 1880 E. Solvay (B. P. 837, of 1880) proposed the employment of calcium chloride for the production of pure gaseous HCl from impure hydrochloric acid. A second patent of his (communicated to W. L. Wise, B. P. 12421, of 1884) prescribes running impure hydrochloric acid into a concentrated boiling solution of calcium chloride, of a boiling-point of 150° or 160°, in such manner that the temperature never sinks below 100°; in this case pure HCl gas escapes. The liquid in this process is stirred either mechanically or by a current of air, which is regulated in such manner that a gaseous mixture suitable for the Deacon process is obtained. This process can be made continuous by running a stream of concentrated hot calcium chloride solution, together with as much impure hydrochloric acid as it is able to decompose, through an apparatus divided into several compartments. In this case there is a continuous evolution of gaseous HCl, whilst the $CaCl_2$ solution runs away, practically free from HCl. Any acid remaining in the $CaCl_2$ solution is neutralised by lime, the solution is concentrated by evaporation and is used over again.

Margueritte's Fr. P. 217005 also describes the purification of hydrochloric acid by $CaCl_2$, but there is no particular novelty about his proposals.

Voster (Ger. P. 50510) proposed passing the roaster-gas, before entering the condensing-apparatus, through a tower in which it meets a fine spray of barium-chloride solution. The temperature in this tower is kept high enough to prevent any condensation of hydrochloric acid.

Lunge and Naef (Ger. P. 52262) proposed expelling the pure HCl from impure roaster-acid by a *current of hot air*, employing just enough air to form a mixture suitable for the Deacon or some analogous process. For this purpose the hydrochloric acid itself must be first heated, and the heat must be as much as possible utilised on the counter-current principle, *e.g.*, by a combination of cisterns with a "hot-air tower." Instead of hot air it is very advantageous to employ the hot gases from blind roasters, which in this case are cooled down to such an extent that they give up their sulphuric acid, together with that contained in the previously condensed roaster-acid. This proposal, very fully worked out on a laboratory scale, was considered to be quite practicable and very advantageous by eminent practical men; but it was not introduced on a large scale, because in the meantime Hasenclever's process (*cf.* below) had been introduced in actual practice, and the few factories in which it could be of any use were unwilling to risk the unavoidable expense and trouble of working out a new process on the large scale.

Whilst none of the processes hitherto mentioned has so far made its way in actual practice, greater success has attended a proposal, first made in 1883 by Hasenclever (B. P. 3393) and again patented in 1888 by the Rhenania Chemical Works (Ger. P. 48280). It is founded on expelling the HCl from impure hydrochloric acid by hot *sulphuric acid.* For this purpose a number of stoneware cylinders, A_1, A_2, A_{10} (Figs. 150 to 152) are connected by pipes *b*. Agitation is produced by mechanical means, or, which is decidedly preferable, by air introduced through the main pipe L at *c*, which together with the HCl at once forms a gaseous mixture suitable for the Deacon process, and is carried off by the pipes *d* either into *e* or into *f*. Pipe *e* serves for the gases directly suitable for the Deacon process, *f* for dilute gases from which the HCl is again recovered. At *g* and *h* crude hydrochloric and sulphuric acid enter, in the proportion of about 100 parts of the former to 550 of sulphuric acid of 142° Tw.; at *i* the sulphuric acid runs away, now diluted to 123° Tw., and is again concentrated to 142° Tw. by evaporation, in order to be used over again. In practice this is done by surface heat.

In actual practice Hasenclever's process is performed in eight or ten stoneware cylinders, about 2 ft. 6 in. wide and 4 ft. high, protected against loss of heat by a wooden jacket, and at the bottom by a lead or cast-iron socket in case of cracking. The sulphuric acid runs in with a sp. gr. of 1·71 (measured cold), and a temperature of about 120°, just as it comes from the top-fired pans, in such quantity that there are seven parts of it to each part of roaster-acid of 30° Tw. The air is injected by a perforated pipe near the bottom.

FIG. 150.

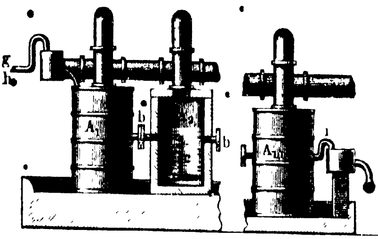


FIG. 151.

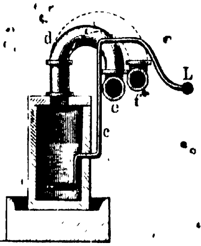
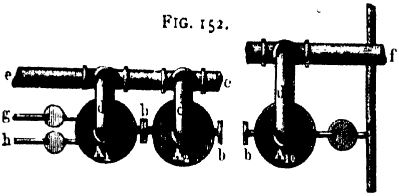


FIG. 152.



The liquid acid mixture flows through the entire set of cylinders, but the gaseous mixture of HCl and air is taken from only half of the cylinders for the Deacon process; the other half merely serves for expelling the small remainder of HCl, which would injure the lead pans in the reconcentration of the sulphuric acid. The HCl expelled here is condensed to weak acid by water, is cooled, and is pumped on to the roaster-acid condenser, where it is again brought to 30° Tw. by fresh gas.

The process goes on perfectly well, and it is even possible to extend it to the pan-acid. This has the advantage of yielding a uniform mixture of air and HCl in proportions exactly suited to the Deacon process, so that the reaction $2HCl + O = H_2O + Cl_2$ can be carried much further than is otherwise possible, giving 84 per cent. conversion instead of 45 per cent. (According to private information received, the strength of the acid does not exceed 6 per cent. HCl.) It is true that the expense of the process is rather great, viz. 16s. per ton of bleaching-powder. The cooling of the dilute hydrochloric acid is also troublesome. The quantity of air must be exactly regulated. This is done by aspirating samples of gas from the exit pipe by means of an india-rubber finger-pump and forcing it through a definite quantity of caustic-soda solution coloured with methyl-orange, until the colour turns pink. The number of charges of the finger-pump should be constant.

E. de Haën (Ger. P. 121886) modifies the process above described as follows:—Muriatic acid, previously freed from arsenic, is run into dilute sulphuric acid, heated 10° above the boiling-point of the former; chemically pure hydrochloric acid, of the same strength as the crude acid employed, distils over. The heating is performed in leaden vessels, by means of a lead steam coil, with steam at three atmospheres pressure. The acid distilling over is condensed in stoneware coils.

Deacon and Hurter (B. Ps. 2104 and 2311, of 1880), with the same object, convey the impure HCl vapours through a tower in which concentrated sulphuric acid is descending. De Wilde and Reychler's patent (17272, of 1889) agrees entirely with this. Another patent of Deacon and Hurter's (15063, of 1888) refers to obtaining dry HCl by the action of a current of air on a mixture of common salt and sulphuric acid.

A. R. Péchiney & Co., have taken out a French patent (No. 217734) for the following process:—The apparatus for expelling pure HCl from crude acid by means of air and sulphuric acid is divided by a perpendicular partition into two unequal compartments, communicating at top and bottom. The smaller of these is provided with several basins; the larger is connected with a sort of Glover tower for reconcentrating the dilute sulphuric acid by hot gases. The hot concentrated sulphuric acid, coming from the bottom of the tower, is mixed with the impure aqueous hydrochloric acid in the top basin of the smaller compartment, flows downward over all the basins, and then enters into the larger compartment, where it is traversed by a current of air which expels the HCl gas, the mixture of gases being used for the manufacture of chlorine.

Solvay & Co. (B. P. 15531, of 1889) employ for distilling HCl a long evaporating-trough, with a longitudinal separation not quite reaching to the back end, and a fireplace underneath the front end. Each of the two compartments is connected by pipes with a smaller, closed trough, placed alongside, and forming the distilling-vessel proper, one pipe serving as an inlet and the other as an outlet. The small trough is not heated. The whole apparatus is filled with sulphuric acid of 142° Tw., or with concentrated calcium chloride solution properly heated. Then by a funnel-pipe hydrochloric acid is run into the small distilling-trough in a continuous jet. Pure HCl is at once given off and escapes by a pipe from the distilling-trough, the water remaining behind and diluting the liquid. In one of the compartments of the long evaporator a paddle-wheel causes the liquid to flow in one direction; therefore the liquid, which is getting diluted in the distilling-vessels, flows slowly through one of the connecting-pipes into the evaporator, travels along the separation, and through the second pipe back into the evaporator, where it is not allowed at once to get to the first (outlet-) pipe, being compelled by zigzag walls to travel a long way between both pipes. The funnel-pipe for feeding the hydrochloric acid is near the second (inlet-) pipe. It is best to employ sulphuric acid, since there is already some in the hydrochloric acid; but in this case the evaporator must be made of lead, whilst with calcium chloride it may be made of wrought or cast iron. [This seems entirely out of the question, as the liquor will never leave the distiller free from acid!]. The distiller must be made of lead, lined with acid-proof stone, or entirely of stone or stoneware.

The principle of making pure HCl from impure acid by expelling it with sulphuric acid is anything but new. As early as 1868 P. W. Hofmann[1] made pure hydrochloric acid on a manufacturing scale by running sulphuric acid of 170° Tw. into crude hydrochloric acid. HCl gas escapes at once, is washed in a washing-bottle, and absorbed in distilled water. This goes on till the sulphuric acid has got down to 131° Tw. It acts of course by attracting water and driving the free HCl off in the state of gas; it is said to retain only 0·32 per cent. HCl. It may either be employed for decomposing salt or be concentrated. One hundred parts of concentrated oil of vitriol furnish 40 parts pure hydrochloric acid of sp. gr. 1·181.

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[1] *Ber.*, ii. p. 272.

As might be expected, Hofmann's process does not remove any arsenic from the hydrochloric acid, but increases it by that derived from the sulphuric acid. In fact Fresenius found the gas contained arsenic in all stages of its evolution. This, therefore, must in any case be removed independently, as will be presently described.

According to a series of patents (Verein Chem. Fabr. of Mannheim, Eng. P. 16910 and 16910 A, of 1906; W. Hasenbach, U.S. P. 834977, of 1906), hydrochloric acid may be freed from arsenic, sulphuric acid, ferric chloride, and all other impurities by washing with hydrocarbon (peat) oils.

Magnesium Chloride is employed by Scheur (Ger. P. 123861). He obtains hydrochloric acid free from sulphuric acid by running crude muriatic acid in a continuous stream into a magnesium chloride solution, boiling at 118° to 120° C., in such manner that the boiling is never interrupted.

Purification of Hydrochloric Acid from Arsenic.

Many proposals have been made for preparing pure, arsenic-free hydrochloric acid from the crude acid. Houzeau[1] states that weak acid can be obtained free from arsenic by simply evaporating it in an open vessel to two-thirds of its volume, in which case all the arsenic distils as $AsCl_3$. In order to obtain a stronger acid, 3 litres of crude acid are put into a 6-litre flask, 0·3 g. of powdered potassium chlorate are added, and the flask is closed by a perforated cork carrying a safety tube and a wide tube of 20 in. length. The latter is drawn out at the bottom and filled with about 100 g. of copper turnings, and on the top of these with a 3-in. layer of asbestos or pounded glass. This tube projects pretty far into the neck of the flask, in order to be heated by the vapours; its upper end is connected, by another tube, with a receiver containing water. If heat is now applied, by the action of the $KClO_3$, the $AsCl_3$ is converted into non-volatile As_2O_5; the excess of chlorine escapes along with the HCl, but is retained by the moist copper, and drops back into the bottle as a solution of $CuCl_2$. In order that an excess of Cl may always be present in the boiling liquid and the reduction of As_2O_5 be avoided, a stream of hydrochloric acid containing ten times the original quantity of $KClO_3$ is run in continuously through the safety-tube. Of course this process is too troublesome and expensive for working on a large scale, and its success is after all only problematical (*cf.* below).

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[1] *Comptes rend.*, lix., p. 1028

A suitable plan for eliminating arsenic was proposed by Bettendorf,[1] viz., adding a solution of stannous chloride in concentrated HCl. This produces a brown precipitate, consisting of arsenic with 1·5 to 4 per cent. of tin, but only in concentrated hydrochloric acid of sp. gr. 1·182 to 1·123: with acid of 1·115 the precipitation is incomplete; with acid of 1·000 no precipitation at all takes place—probably because then the arsenic is not present in the liquid as $AsCl_3$, but as As_2O_3. This reaction is not only very well adapted for detecting arsenic in the presence of antimony, since the latter is not acted upon by $SnCl_2$, but also for purifying crude muriatic acid from arsenic, which is precipitated by a fuming solution of $SnCl_2$, separated by filtration after twenty-four hours and the acid distilled off almost to dryness. The distillate is quite free from arsenic. Probably, instead of distilling, Hofmann's process of driving out the HCl in the cold by strong vitriol might be employed, if the latter can be obtained free from arsenic.

Mayerhofer[2] completely confirmed Bettendorf's statements, but found that mere oxidation of $AsCl_3$ to As_2O_5 and subsequent distillation could not purify the hydrochloric acid from arsenic, as H. Rose and others had asserted; for arsenic acid is decomposed by HCl, especially on heating, with formation of $AsCl_3$ and chlorine, and that all the more easily the more concentrated the HCl. Hence the proposal made by Bensmann[3] according to which the acid is to be diluted to sp. gr. 1·12 and distilled with potassium chlorate, cannot produce the desired result.

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[1] *Dingl. polyt. J.*, cxciv, p. 253. [2] *Anal. Chem. Pharm.*, clviii., p. 326.
[3] *Chem. Zeit.*, 1883, p. 203.

The Harkortsche Bergwerke und Chemische Fabriken (Ger. P. 109488) bring the *gaseous* (impure) HCl into contact with a solution of stannous chloride, either by passing it through the solution contained in a suitable vessel, or upwards in a tower in which the solution is running down. The purification takes place most quickly if the temperature of the stannous chloride solution is not much above that of the outer air.

Hager[1] remarks that, if the precipitate formed in Bettendorf's process is not completely filtered off before distillation, the distillate always contains arsenic, even with an excess of stannous chloride. From the latter stannic chloride is formed

$$(3SnCl_2 + 6HCl + As_2O_3 = As_2 + 3H_2O + 3SnCl_4),$$

and passes over into the distillate. Hager consequently recommends the process of Duflos:—The acid is diluted to 1·13 sp. gr.; if it contains any SO_2, some MnO_2 (or $KClO_3$) is added then broad bright strips of copper are put in and digested one day at about 30° C. The strips of copper are taken out scoured, and put into the acid for another twelve or fourteen hours. Thus all the arsenic is precipitated on the copper, the chlorine is removed, and the ferric chloride is reduced to ferrous chloride. Thallium also is precipitated by copper in the presence of arsenious acid. The liquor is then distilled, after first putting a few scraps of copper into the retort, in order to protect the ferrous chloride against being reconverted into ferric chloride.

Diez accomplishes the same result by treatment with sulphuretted hydrogen, filtering, and distilling;[2] Engel,[3] still more simply, by adding 0·04 to 0·5 per cent. potassium thiosulphate, pouring off from the precipitate, and distilling.

The Tentelev Chemical Works (Eng. P. 107312 of 1916) obtain pure hydrochloric acid by distilling the commercial acid in the presence of a concentrated solution of zinc chloride of such strength that it may be heated to 125° to 135° C. The operation is continuous, crude acid being introduced in quantity equivalent to the pure acid obtained.

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[1] *Wagner's Jahresber.*, 1872, p. 263.
[2] *Wagner's Jahresber.*, 1873, p. 263.
[3] Engel, *ibid*, 187[illegible], p. 275.

Hargreaves and Robinson (B. P. of 29th Aug. 1872) proposed to add H_2S before condensation in the manufacture of HCl on the large scale, in order to remove arsenic and to reduce SO_2 to S. The latter was of special importance to them, as in their process the HCl always contained a little SO_2, which was prejudicial in the preparation of chlorine.

Leather (B. P. 2493, of 1882) treats hydrochloric acid with *barium sulphide*, which removes both arsenic and sulphuric acid. D'Andria (B. P. 17908, of 1887) employs precipitated zinc sulphide. Beckurts[1] removes arsenic by distilling hydrochloric acid with ferrous chloride and rejecting the first 30 per cent. of the distillate, which contains some arsenic, whilst the subsequent 60 per cent. is free from it. Otto[2] saturates the acid, after diluting to sp. gr. 1·12, by repeated treatment with H_2S, separates from the precipitated As_2S_3, distils, removes the first portions of the distillate, and collects nine-tenths of the acid as pure.

Whitehead and Gelstharp (B.P. 18940, of 1894) treat the crude muriatic acid with sulphuretted hydrogen or preferably with a mixture of H_2S, SO_2, and air, such as is obtained by the action of muriatic acid on Leblanc soda refuse.

Wylde, Kynaston, and The United Alkali Co. (B. P. 11353, of 1897) purify hydrochloric-acid gas from arsenic by cooling it and passing it through a drying tower filled with coke, where the arsenic is entirely retained.

The Farbwerke Hochst (Ger. P. 167355) remove the arsenic by vanadious salts. They pass the hydrochloric acid gases through the blue solution of vanadious hydrochloride or sulphate, which thereby turns green, the reduced arsenic being separated as a powder. This also retains the chlorine and ferric chloride. The inactive, green solution is freed from the arsenic by filtration, and vanadium protoxide is reduced from the V_2O_3 by electro-chemical methods.

A similar process was also patented by the Farbwerke vorm. Meister Lucius und Brüning (Ger. P. 164355, of 1914).

The Verein Chemischer Fabriken in Mannheim (Ger. Ps.

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[1] *Fischer's Jahresber.*, 1884, p. 348; 1887, p. 545.

[2] [illegible] r., 1886, p. 1001.

179513, 179514, and 187325) have found that *mineral oils* take up the arsenic from gases and liquids, if they are brought into intimate contact with them, preferably also applying a cooling action. If the arsenic is not already present as As_2Cl_3, it is brought to this state, *e.g.*, in dilute muriatic acid by passing some gaseous HCl into it, and in sulphuric acid containing arsenic by the same means. The mineral oil employed (*e.g.* lignite oil) is not chlorinated itself, if the temperature remains low, and can be regenerated by washing, first with lime water and then with hydrochloric acid. From ordinary hydrochloric acid the arsenic may be removed by agitating with mineral oil, and in the same way from sulphuric acid by adding some muriatic acid, which transforms the arsenic into chloride, and subsequently agitating with mineral oil. (The British patents for this purpose have been taken out by C. W. Johnson—Nos. 16910 and 16910 A, of 1906.)

The same firm in their Ger. P. 195437 (B. P. by Johnson as above; Fr. P. 368752) extend the process to other oily matters, excluding easily decomposable glycerides of fatty acids. They also propose cooling down the liquids before bringing them into contact with the oils.

Dr Lunge was informed that these processes have proved quite efficient, and are in constant application in Germany, England, Austria, and the United States.

The Chemische Fabrik Griesheim-Elektron (Ger. Ps. 194864 and 195578) removes the arsenic by dichlorbenzene or carbon tetrachloride, or, preferably in the case of gases, by acetylene tetrachloride, allowing the gases to meet these liquids in towers. The washing-agents are entirely freed from arsenic by washing with about twice their bulk of water.

Arsenic and most other impurities may be removed[1] by passing the dry gas through a brine circulating refrigerator which condenses the arsenious chloride and other impurities.

Lucron and Riche (Fr. P. 480247, of 1915) convert the impurities into non-volatile compounds by addition of permanganates or other per-salts and obtain the pure HCl by distillation.

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[1] Le Roy, *Chem. Trade Journ.*, 1913, p. 435.

Removal of all Impurities from Hydrochloric Acid.

Sulphurous acid and chlorine, according to Domonte, are removed from hydrochloric acid by a current of carbonic acid, without reducing its percentage of HCl. The latter assertion has been refuted by Roscoe and Dittmar, the former by Bolley and Ott, who did not notice the least effect of carbonic acid on the SO_2 contained in hydrochloric acid.[1]

Chemically pure acid for pharmaceutical purposes is said by Giudice[2] to be prepared by removing from the sulphuric acid, previous to its decomposing the salt, any SO_2 by potassium bichromate or permanganate, and passing the HCl through mercury, in order to remove Cl, Br, I, and $FeCl_2$ [but this result can hardly be attained in this manner!]

Friese[3] holds that perfectly pure hydrochloric acid can be made from common salt and ordinary sulphuric acid by thoroughly washing the acid gas with boiling water or steam before passing it into the absorbing-vessels

Habermann[4] prepares perfectly pure hydrochloric acid from *so-called* pure acid of commerce by adding 0·5 g. potassium chlorate to a litre of it and distilling from a glass retort with a Liebig cooler into a receiver, containing so much distilled water that an acid of from 20 to 25 per cent. HCl is formed when ¾ of the contents of the retort have distilled over. If free chlorine is to be excluded as well, the receiver is changed when the distillate comes over entirely colourless. All the arsenic is said to remain in the residue.

A *gas-filter* for the purification of hydrochloric acid is described by Boulouvard (B. P. 4609, of 1899). A tank is provided with a kind of grate, formed by coarser particles, on which rests a layer of 18 in. to 3 ft. depth, formed of grains of ⅛ to ¼ in. diameter of indifferent substances (coke, quartz sand, crushed stoneware, with a rough surface on which dusty and fog-like particles of salts, arsenious chloride, ferric chloride, selenium, and sulphuric acid are retained). The gases pass the tank slowly from the top downwards, say about 1 cbm. per 0·5 sq. m. of surface. (Similar gas-filters are employed by Kessler in the concentration of sulphuric acid, and in the plate-tower erected at Duisburg, *supra*, p. 325.) Sometimes such a gas-filter will certainly cause such a loss of draught, that artificial draught will have to be created either before or behind the filter.

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[1] *Wagner's Jahresber.*, 1860, p. 192.

[2] *Fischer's Jahresber.*, 1882, p. 373.

[3] *Chem. Ind.*, 1896, p. 987.

[4] *Z. angew. Chem.*, 1897, p. 202.

Skinner (U.S. P. 875558) allows the crude muriatic acid to run into distilling flasks from which the vapours pass into a large intermediate vessel where ferric chloride and the other impurities are separated, except chlorine. The gas is removed by bringing the vapours into contact with acetylene gas. (Arsenious chloride will not be removed in this way.)

Injurious Effects of the Impurities of Hydrochloric Acid.

The presence of *sulphuric acid* is very injurious in the revivifying of the spent char of sugar-works by forming calcium sulphate, which stops up the pores and on ignition is converted into calcium sulphide. According to Deutecom[1] such acid cannot be employed in carbonising wool, because it acts too strongly on the iron drums. In the manufacture of sal-ammoniac and of aniline hydrochloride it interferes with the crystallisation. In dissolving basic slag (from the Thomas Gilchrist process) it acts less advantageously than pure hydrochloric acid. Rurup[2] states that in galvanising iron impure acid causes black spots which do not take the zinc. For galvanising purposes the acid ought not to contain upwards of 1 per cent. SO_3; 1·5 per cent. is the extreme limit.

Sulphurous acid is easily reduced to H_2S, which acts strongly on brass wire-netting, and causes inequalities if used for pickling iron before rolling it into sheets. *Arsenic* acts similarly. Its presence has, moreover, caused fatal accidents; acid containing arsenic has been used for producing hydrogen. *Nitric* and *nitrous acid*, *chlorine*, and *selenium* are injurious in the manufacture of aniline hydrochloride, which thereby acquires a red and afterwards a greenish colour. Selenium also produces a pink shade in sal-ammoniac. According to G. E. Davis,[3] it is the presence of selenium which makes the acid unsuitable for refining oil, pickling wire, bleaching, etc.—not iron or arsenic, as commonly supposed

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[1] *Chem. Zeit.*, 1892, p. 57

[2] *Chem. Zeit.*, 1894, p. 225.

[3] *J. Soc. Chem. Ind.*, 1883, p. 157.

Packing and Conveying Hydrochloric Acid.

Until a few years ago the carriage of hydrochloric acid was very troublesome, because manufacturers confined themselves much longer to the exclusive use of glass carboys, packed in wicker hampers or wooden tubs, than in the case of sulphuric acid, under the impression that this was unavoidable. In the case of hydrochloric acid, with its lower specific gravity, the dead weight to be carried and the loss by breakage of the carboys is comparatively even more serious than in the case of sulphuric acid, which, moreover, formerly represented a greater value. In France glass carboys were, in fact, frequently replaced by earthenware bottles, of Beauvais pottery, holding about as much as the glass carboys (say, 11 or 12 galls.); these could be stored up loose at the works, but when being sent away, they were also put in hampers. Sometimes even smaller packages were used, such as bottles holding about 45 lb., four of which were packed in a case.

The early attempts at doing without glass carboys were not very successful, so long as vessels of not much larger size were employed. Thus, for instance, in England gutta-percha bottles, holding 1½ or 2 cwt., were sometimes employed; but these cost £3 each, which was about fifteen times as much as the acid contained in them, and they required constant repairs. Of course they could only be employed for sending to comparatively short distances, as they had always to be returned to the works.

Iron vessels with ebonite lining, as shown in Fig. 153, are much better. At *a*, the india-rubber hose for running-off is shown. These vessels hold about 8 tons, and none but these are used at the Chauny works.

In Germany mostly stoneware vessels, of the shape shown in Fig. 157, are now employed. Such pots, of a capacity of 800 litres (about 180 gallons) have a height (without cover) of 4 ft. 3 in., and an outside width of 3 ft. 6 in. Twelve of these are placed on a railway truck, 23 ft. 9 in. long and 8 ft. 3 in. wide, in two rows, and are firmly fixed thereon by a wooden frame, the bottom and all contact surfaces being protected by felt against the effect of shocks. These twelve pots contain 10 tons of acid. They are fixed on a truck, and are filled and emptied by siphons.

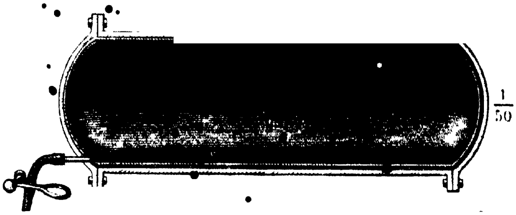

FIG. 153.

As these hydrochloric-acid railway trucks must be constructed in a particular manner if they are to fulfil their object, and as there appears to be some difficulty in obtaining

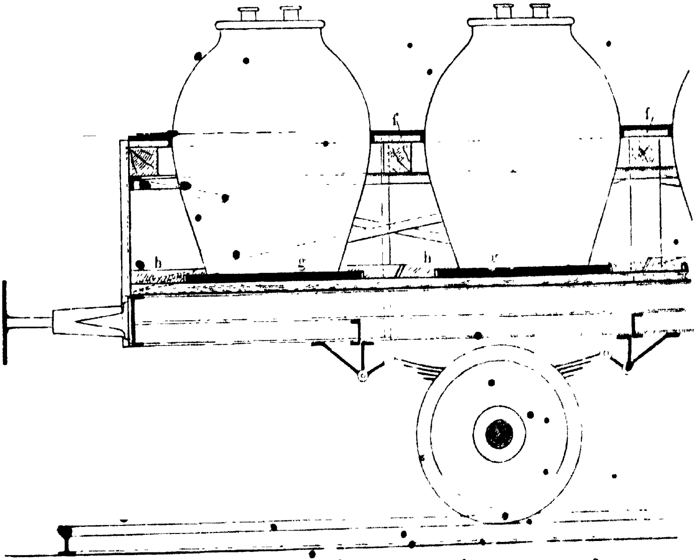

FIG. 154.

particulars on this point, such a truck is shown with all details in Figs. 154 to 157. Fig. 154 is a longitudinal section; Fig. 155 sectional plans at levels *a* and *b* in Fig. 154; Fig. 156

a cross-section; Fig. 157 a half-section of one of the pots. We notice the wooden blocks *f f*, coated at both ends with india-rubber or felt, by which the pots are stayed against one another; on the top they are kept together by light boarding, *e e*; *g g* are linings for the bottoms of the pots, made of cork wood; *h h* are wooden blocks, staying the pots at their

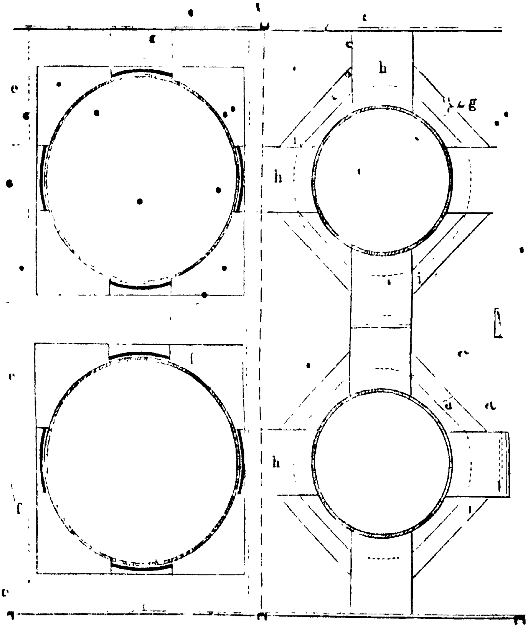

Fig. 155.

lower part, without india-rubber lining, fixed by the cross pieces *i i*. In Fig. 157 we see the joint, made for being stemmed with coal-tar and sulphur.

Pohl (Ger. P. 30'188) proposes coating iron vessels with asbestos cloth soaked with paraffin, wax, stearine, and the like, for the purpose of carrying acids. Kramer (B. P. 4684, of 1895) employs wooden vessels coated inside with asbestos and

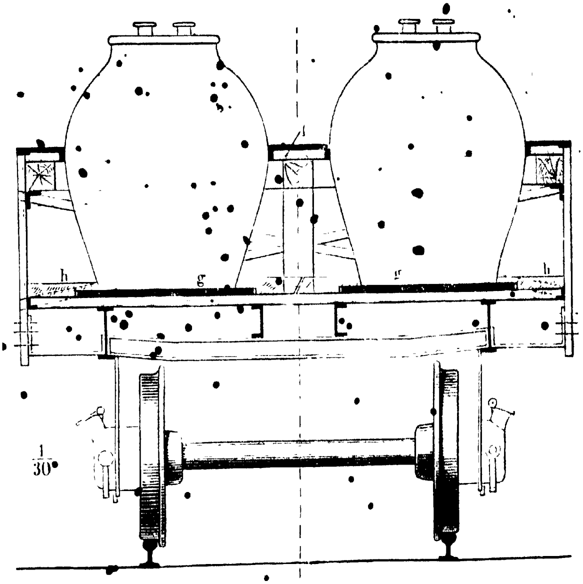

Fig. 156.

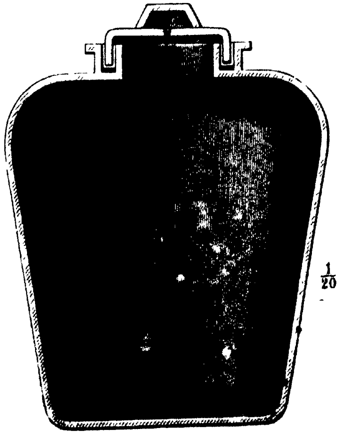

Fig. 157.

silicate of soda, and afterwards with paraffin, wax, pitch, tar, etc.

Simonet (Ger. P. 6437) places carboys of acid-resisting material in a metallic jacket consisting of two halves; the space between the carboy and jacket is filled with some suitable substance.

Some of the apparatus and contrivances for conveying sulphuric acid, described sulphuric acid volume, will also serve for hydrochloric acid.

Pfeffer[1] discusses at length the carriage of chemical liquids on railways.

A description of the truck for the carriages of muriatic acid by Charles Roberts & Co., of Horbury Junction, Wakefield, is given.[2] It is a truck, holding 10 tons acid, made of wood, avoiding any iron nails and screws and the like, and thoroughly coated with pitch and tar.

In Germany, railway cars are built holding 15½ tons acid, stored in vessels with nearly straight sides, of a capacity of 11 or 12 cwt. each.

A carefully designed tank for the transport of hydrochloric acid by road, rail, or water is patented by British Dyes Limited, J. Turner and J. H. West (Eng. Pat. 124, 997). The tank is built up of steel plates lined with ebonite or vulcanite, vulcanised on to the metal. The method of jointing, baffling, and air-escape are described.

Storing Cisterns for Hydrochloric Acid.

Usually *stone cisterns* are employed, which have been described on pp. 261 *et seq.*: but these are heavy and expensive. In many cases *stoneware pots* (pp. 270 *et seq.*) may be used, especially by connecting a number of them, by means of glass, india-rubber, or stoneware siphons, in such manner that the acid can be run in or out of any one of the vessels.

Round wooden store vessels are shown, Fig. 118, p. 316; they are not often met with. A better plan is that of *square wooden cisterns*, lined with brick, joined with coal-tar asphalt; the well-known cement made of asbestos powder and dilute water-glass solution is also applicable here.

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[1] *Z. angew. Chem.*, 1908, pp. 98 *et seq.*

[2] *Chem. Trade Jour.*, 1908, vol. xlii., pp. 6[illegible] *et seq.*

T. D. Owens (B. P. 21294, of 1892) makes hydrochloric-acid cisterns of two layers of wood or other material, with an intermediate space into which is poured a molten mixture of about equal parts of brimstone, ground pyrites, and sand. The inner wooden shell may be left out, and the above mixture applied on a background of wood, slate, vulcanite, or metal This invention is also applicable to the construction of electrolytic cells, vitriol chambers, condensing towers, etc.

The Deutsche Ton-, und Steinzeugwerke, Charlottenburg, supply iron-cased stoneware vessels, consisting of single pieces joined by an acid-proof cement

Adamson (U.S. P. 846541) employs bottles of glass, ceresine, or other materials, the bottoms and sides of which are strengthened by wire gauze embedded in the material.

The Westdeutsche Tonwerke at Euskirchen make stoneware vessels up to 10 tons capacity, and weighing less than the stone cisterns. Stoneware vessels holding up to 2½ or 3 tons capacity are now made by all larger potteries, and are found at all German works.

Statistics.

Exact statistics as to the quantity of hydrochloric acid manufactured cannot be obtained in most cases, as most of it is employed at once for making chlorine, etc. It may be indirectly, but only very imperfectly, inferred from the amount of salt decomposed; *cf.* p. 21.

For Germany, Hasenclever estimated the production in 1882:—

From 18 soda-works =	126,450	tons acid, 20° Baumé.
„ 8 potash „	22,000	
	148,450	

In 1891, Germany imported 481, and exported 1031 tons hydrochloric acid.

France imported in 1893, 3812 tons hydrochloric acid and exported 1517 tons.

O. N. Witt[1] calculates the German production of saltcake and muriatic acid at 300,000 tons each in 1902. For 1906 we may put the figure = 350,000 to 400,000 tons each. The exportation in 1901 amounted to 41,742 tons saltcake and 12,143 tons muriatic acid.

Some statements on the production of muriatic acid in Russia are found in *Chem. Ind.*, 1900, p. 543, and *Chem. Zeit.*, 1900, p. 313.

Belgium produced 22,500 metric tons of hydrochloric acid in 1913, and 27,000 metric tons in 1929.

Only for the United States do we possess accurate statistics in the *United States Census Bulletin*, No. XIII., by Professor Chas. E. Munroe. From this we take the following statements:—

	In 1900	In 1905.
Number of factories manufacturing muriatic acid	31	36
Of these there were principally occupied with other products	18	25
Quantity of muriatic acid produced . . lb.	134,229,012	188,538,396
Value of this . . . . dollars	1,173,900	1,730,221
Of this there was worked up in the factories themselves . . . . lb.	17,553,903	61,035,714
Average value of 1 lb. in cents . . .	0·0087	0·0092

HCl manufactured in U.S.A. in 1914 (Dept. of Commerce, Misc. Rep., No 82, p. 177):—

	Short Tons.	Value.
HCl manufactured for sale . .	85,438	$1,343,805
Made and consumed . . .	83,145	...
Total production . . .	168,584	...

The condensation in Woulfe's bottles and coke-towers has been replaced there in most cases by Lunge-Rohrmann columns. The Cellarius touries are also employed.

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[1] *Chem. Ind. d. Deutsch. Reiches*, 1902, p. 82.

Applications.

The *applications of hydrochloric acid* are extremely numerous. Some of it serves for preparing chlorine, which, in its turn, is employed for manufacturing bleaching-powder and liquor, chlorate of potash, etc., or directly for bleaching. In Germany, during the year 1878, the stoppage of several alkali works raised the price of hydrochloric acid so much that in some places the manufactures of chloride of lime and other applications of that acid at the works themselves were discontinued.

The growth of the electrolytic alkali process has made chlorine more plentiful than hydrochloric acid. Each is now made from the other, according to which is the more plentiful in the district.

The application of *weak* HCl have been described on p 368. Hydrochloric acid further serves, mostly in its ordinary state of concentration, for preparing the chlorides of zinc, tin, antimony, ammonium, barium, calcium, etc.; for manufacturing bone-glue, superphosphate, purified animal charcoal; for revivifying bone-char; for bleaching, partly by itself, partly along with chloride of lime, and in innumerable cases in dyeing and printing; for preparing several other acids, especially carbonic acid (in the manufacture of sodium bicarbonate, mineral waters, etc.); for neutralising the caustic soda in manufacturing alizarine and resorcine, and in the manufacture of many other artificial colouring-matters; for pickling iron and zinc; for freezing-mixtures (with Glauber's salts and snow); for preparing lead oxychloride from galena by Pattison's process; for making aqua regia; for purifying sand and clay from iron for glass and ceramic manufactures; for purifying cream of tartar; for precipitating fatty matters from soap-suds, and for decomposing the lime-soap formed from the same, for the metallurgical preparation of copper, and of galena containing zinc; for getting the zinc from tinplate scraps; for recovering sulphur from tankwaste; for removing boiler-scale; as auxiliary in diffusion at beetroot-sugar works;[1] for saturating the syrups and the manufacture of sugar from molasses by means of alcohol; and for innumerable other purposes.

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[1] *Dingl. polyt. J.*, ccxxi., p. 92.

A very interesting guide to the relative demands for hydrochloric acid in various industries is given by Munroe[1] from data collected by the U.S. Bureau of the Census

	Hydrochloric Acid.	
	1900.	1905.
	lb.	lb.
Production	134,229,012	188,538,396
Consumption :—		
Bleaching materials	908,000	1,004,000
Chrome tannage	5,000,000	6,000,000
Cleaning facades	3,000,000	4,000,000
Disinfectants	2,500,000	3,200,000
Dyestuffs	6,559,464	7,632,027
Fine chemicals	1,146,692	1,181,078
General chemicals	3,488,000	13,096,827
Glucose making	10,846,828	12,283,466
Glue making	38,186,338	61,795,150
Olive curing	2,500,000	3,500,000
Papermaking	3,000,000	4,000,000
Pickling metals	27,000,000	30,000,000
Reducing and refining metals	15,357,680	24,729,290
Soapmaking	400,000	393,246
Soldering	4,000,000	3,000,000
Textiles	6,000,000	7,000,000
Washing bone black	1,500,000	1,750,000
Washing sand and clay	1,500,000	2,000,000
All other uses	1,336,005	1,973,312

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[1] *J. Washington Acad. Sci.*, 1911, 1, 70.

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